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Electrochemical reduction of CO₂ and H₂O into fuels: Cell types and kinetic barriers

Mogens B. Mogensen, Professor at DTU Energy Conversion

Presented in:

Electrocatalysis of Energy Generation and Storage

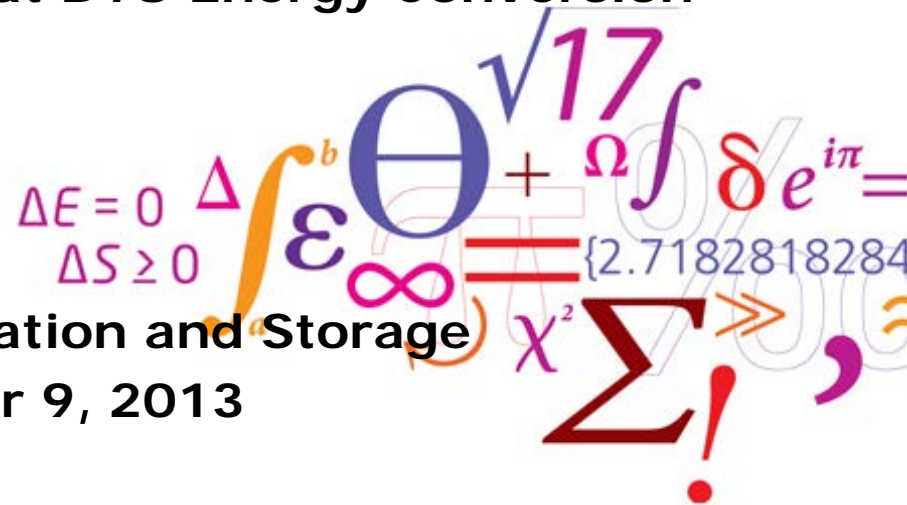
– AM Session Monday, September 9, 2013

246th ACS National Meeting

Indianapolis, Indiana, USA

DTU Energy Conversion

Department of Energy Conversion and Storage



DTU = Technical University of Denmark

- Sustainable technologies for energy conversion and storage
- Located on two campuses near Copenhagen, Denmark: Risø and Lyngby
- 230 employees – ca. 100 in electrochemistry
- Our research span from fundamental investigations to component manufacture
- Focus on industrial collaboration and industrially relevant processes



DTU Energy Conversion, Technical University of Denmark



Outline

1. Introduction
2. Motivation and need for electrolysis
3. Vision
4. Types and status of electrolyzer cells
5. Electrocatalysts and kinetics in various electrodes
6. Barrier modeling problems
7. Concluding remarks

Introduction

- There are clear reasons to look for means of promoting fluctuating renewable energy, e.g. photovoltaics and wind turbines:
- Probable anthropogenic climate change by CO₂ emissions
- Limited supply of cheap fossil fuel resources in the long term
- Security of supply and geopolitical consequences of unequal distribution of resources
- Synthetic fuels – CO₂ neutral “green” hydrocarbon fuels - seem particularly benign to replace the fossil fuels.

What to do? – The Danish answer: Energy plan for Denmark

1. 2020: 50 % electricity from Renewables
2. 2035: 0 % fossil energy in power and heat production
3. 2050: 100 % renewable energy

Challenges

- 1) Increasing share of fluctuating production
- 2) Liquid fuels will still be needed; biomass is limited

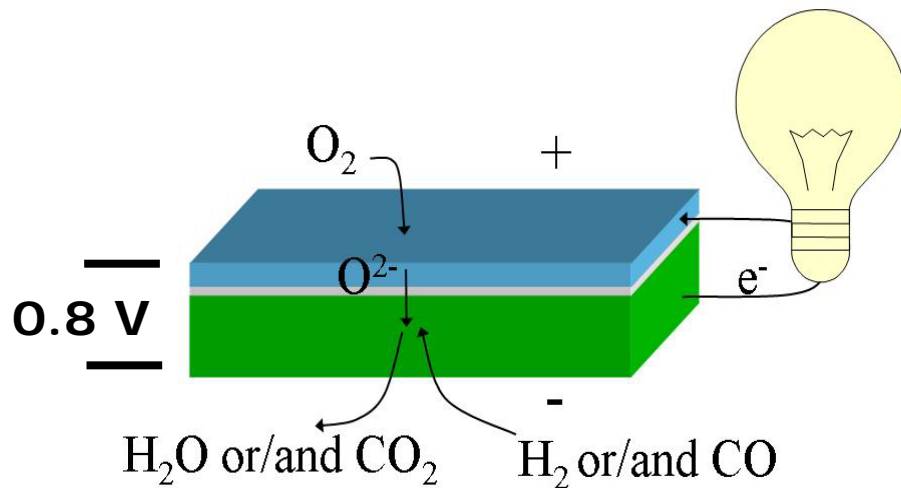


Electrolysis is needed

- Many conversion and storage technologies:
 - Pumping of water to high altitudes
 - Batteries
 - Flywheels
 - Superconductor coil (magnetic storage)
 - **Electrolysis – Electrochemical reduction of H_2O and CO_2**
 - Thermo-chemical looping
 - Solar Thermal Electrochemical
 - Photo-electrochemical HER and CO_2 reduction
- All are very important! But: first 4 are not for long distance (> 500 km) transport. 3 last are early stage research - may prove efficient in the future.
- Therefore, within a foreseeable future: **Electrolysis will become necessary in order to get enough renewable fuels!**

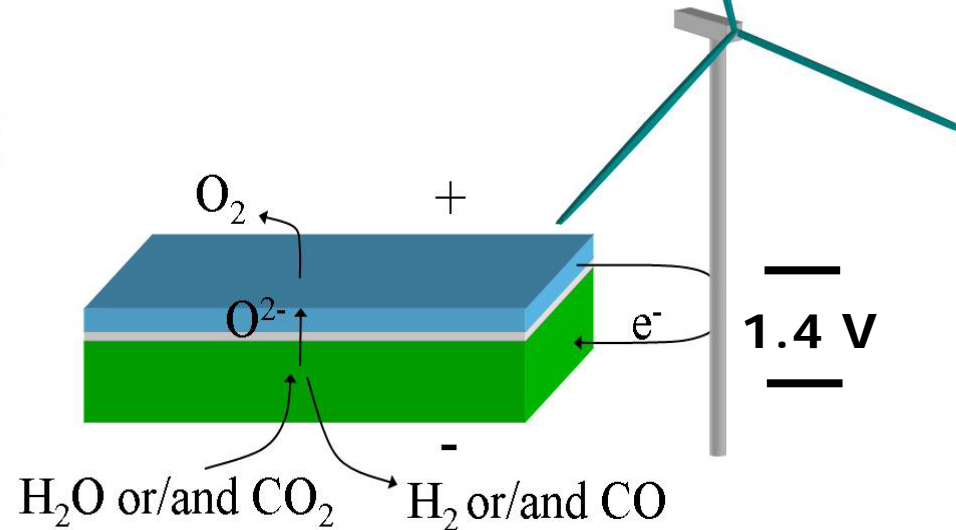
Principle – Solid Oxide Cell as example

A SOFC



750 - 850 °C

B SOEC



EMF ca. 1.1 V

Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

Production of syngas

Reaction scheme :

The overall reaction for the electrolysis of steam plus CO₂ is:



This is composed of the three partial reactions(for SOEC case): At the negative electrode:



and at the positive electrode:



Emphasis on oxygen evolution reaction (OER) at low temperatures – this is by far the slowest reaction

$2 \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2 (+ \text{H}_2\text{O})$ is also possible

Synthetic fuels from syngas: why?

The power density argument

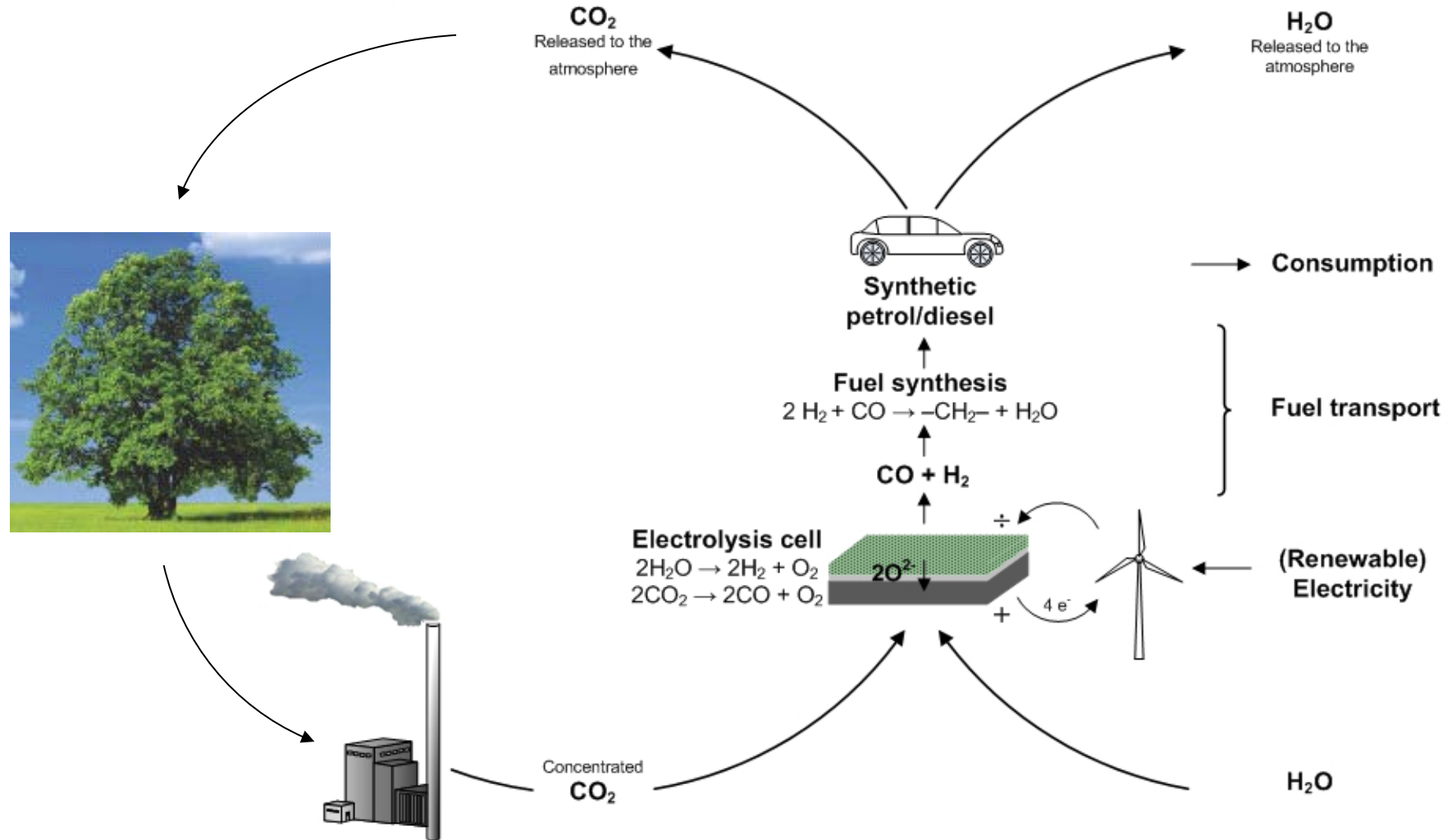
- Syngas ($H_2 + CO$): all kinds of synthetic fuel using existing catalysts
- If renewable energy used for electrolysis, the fuel is CO_2 neutral!
- Gasoline filling rate of 20 L/min equivalents 11 MW of power and means it takes 2½ min to get 50 l = 1650 MJ on board
- Li-batteries: 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.
- The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.

Visions for synfuels from electrolysis of steam and carbon dioxide

1. Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).
2. Large SOEC systems - produce DME, gasoline and diesel - Iceland, Canada, Greenland, Argentina, Australia ... geothermal, hydro, solar and wind.
3. Target market: replacement of natural gas and liquid fuels for transportation
4. All the infrastructure exists!!

Vision, Biomass CO₂ recycling

Short term realisation - CO₂ capture from industrial sources



Electrolysis and Fuel Cell Types - reversibility

1. Simple aqueous electrolytes (e.g. KOH or K_2CO_3), room temperature to ca. 100 °C, 0.1 - 3 MPa pressure. The classic versions of alkaline electrolyser and fuel cell are not directly reversible. Low gas solubility in electrolyte.
2. Low temperature “solid” proton conductor membrane (PEM), 60 – 80 °C, and high temperature PEM 120 - 190 °C. Not directly reversible due to materials issues
3. Immobilized aqueous K_2CO_3 , Na_2CO_3 , KOH in mesoporous structures, solid acids etc. – pressurized 200 – 300 °C, 0.3 – 10 MPa. Probably directly reversible.
4. Molten carbonate electrolytes, fuel cells 650 °C; electrolyser 800 – 950 °C, 0.1 MPa. Electrolytes have very different compositions, so not directly reversible. Only CO_2 electrolysis.
5. High temperature solid oxide ion conductor (stabilized zirconia), 650 – 950 °C, pressurized 0.5 – 2 (5?) MPa. Reversible!

Electrolysis cell type status

- Few types commercialized but - from an energy conversion and storage point of view - none of them are commercial in today's energy markets.
- The classical alkaline electrolyser was commercialized during the first half of the 20th century and is closest to market today, but still too expensive.
- If significant amounts of synfuel via electrolysis in the very near future (the next 1 -5 years) – only the classical alkaline electrolyzers is available on some scale – but still relatively limited.
- SOC clearly has a very high potential as reversible fuel cell – electrolyser cell
- New types are under investigation

Electrocatalysis and definition of an electrocatalyst

An electrocatalyst is a catalyst that participates in an electrochemical reaction in an electrode of an electrochemical cells but not consumed

Usually only interested in the electrocatalyst that improve electrode kinetics

Electrocatalytic activity varies with varying electrode potential vs. a reference electrode

Alkaline Electrolysis cells

- The electrolyte is usually ca. 30 wt% KOH in water
- Relative inexpensive electrocatalysts; Ni, MoOx for HER, NiO, CoOx, Ag for OER
- Cathode (negative electrode) reaction:
$$2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$$
- Anode (positive electrode) reaction:
$$2 \text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^-$$
- Total: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
- Very simple reaction, which in practice may run at temperatures down to 60 °C
- Only H₂ production

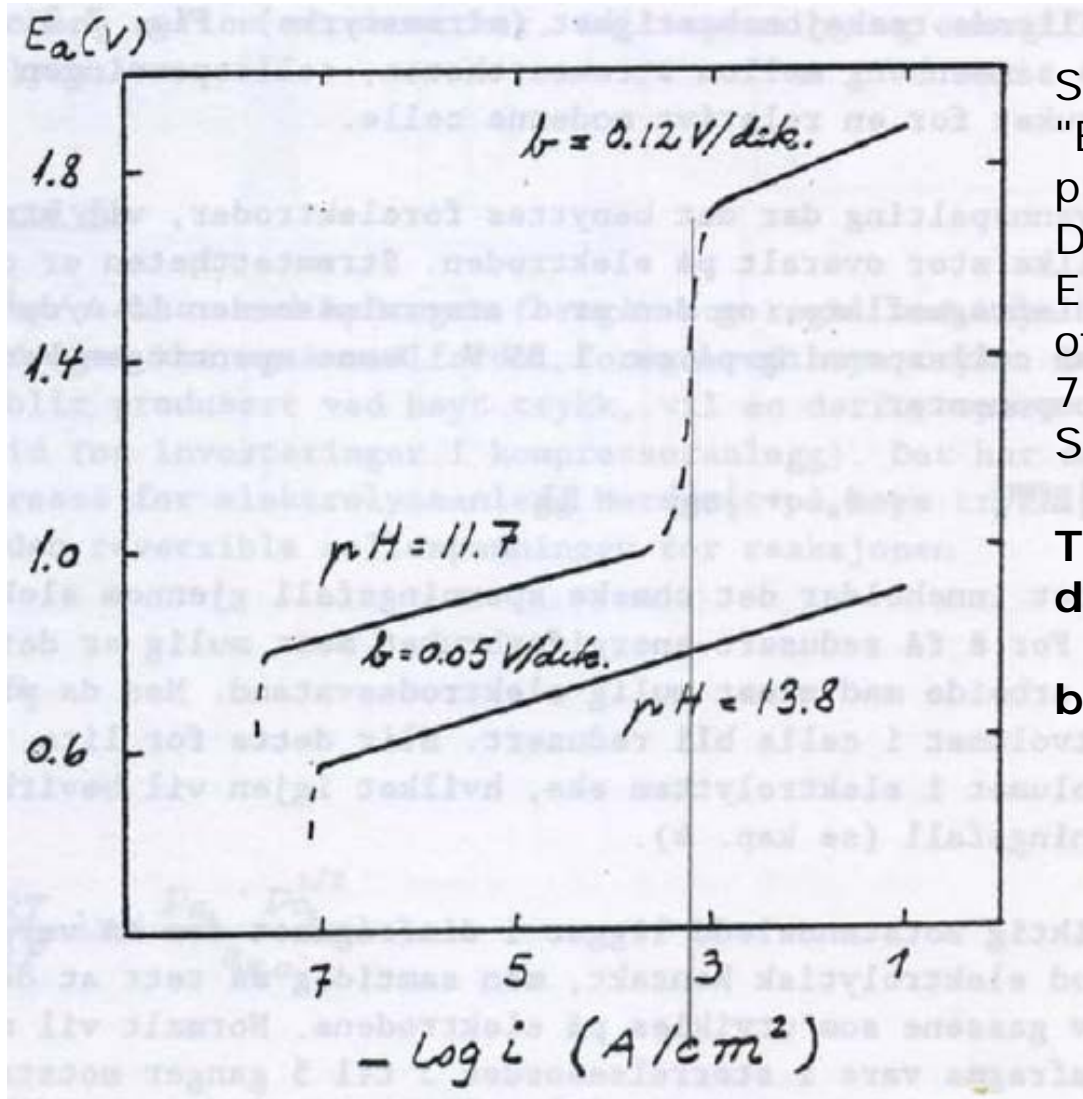
PEM

- The main advantage of polymer membrane fuel cell and electrolyser cell is that it is compact and operates at 60 – 80 °C, making the balance of plant relatively inexpensive.
- Main problem is cost of cell and stack materials, in particular in case of the electrolyser.
- The oxygen electrode cannot use the carbon support used in the PEMFC – expensive Ti alloys are used instead.
- Only expensive electrocatalysts, Pt for HER, Pt or IrO₂ for OER
- Only H₂ production

Electrocatalysis - A PEM problem

- It is well-known that both H_2 and O_2 electrodes are very sluggish at temperatures below 100 °C and not fast until above ca. 200 °C in acid electrolytes
- However, a lot of confusing data have been reported
- O_2 evolution as a function of pH as example:

Oxygen evolution vs pH



Source: Jomar Thonstad:
 "Elektrolyseprosesser/Electrolysis processes", Lecture notes,
 Department of Industrial
 Electrochemistry, Norwegian Institute
 of Technology (NTH/NTNU) (1991) p.
 7-5A. Provided to me by Svein
 Sunde, NTNU, April 2013.

**The vertical line indicates a
 diffusion limiting current density.**

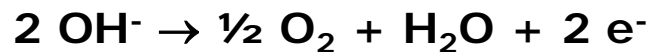
b – values are Tafel slopes

Oxygen evolution vs pH

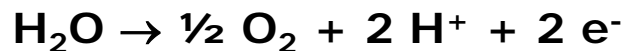
The NTNU data is interpreted as follows:

The diffusion limited species is OH^-

At low current density or high pH the OER is reduction of OH^- :



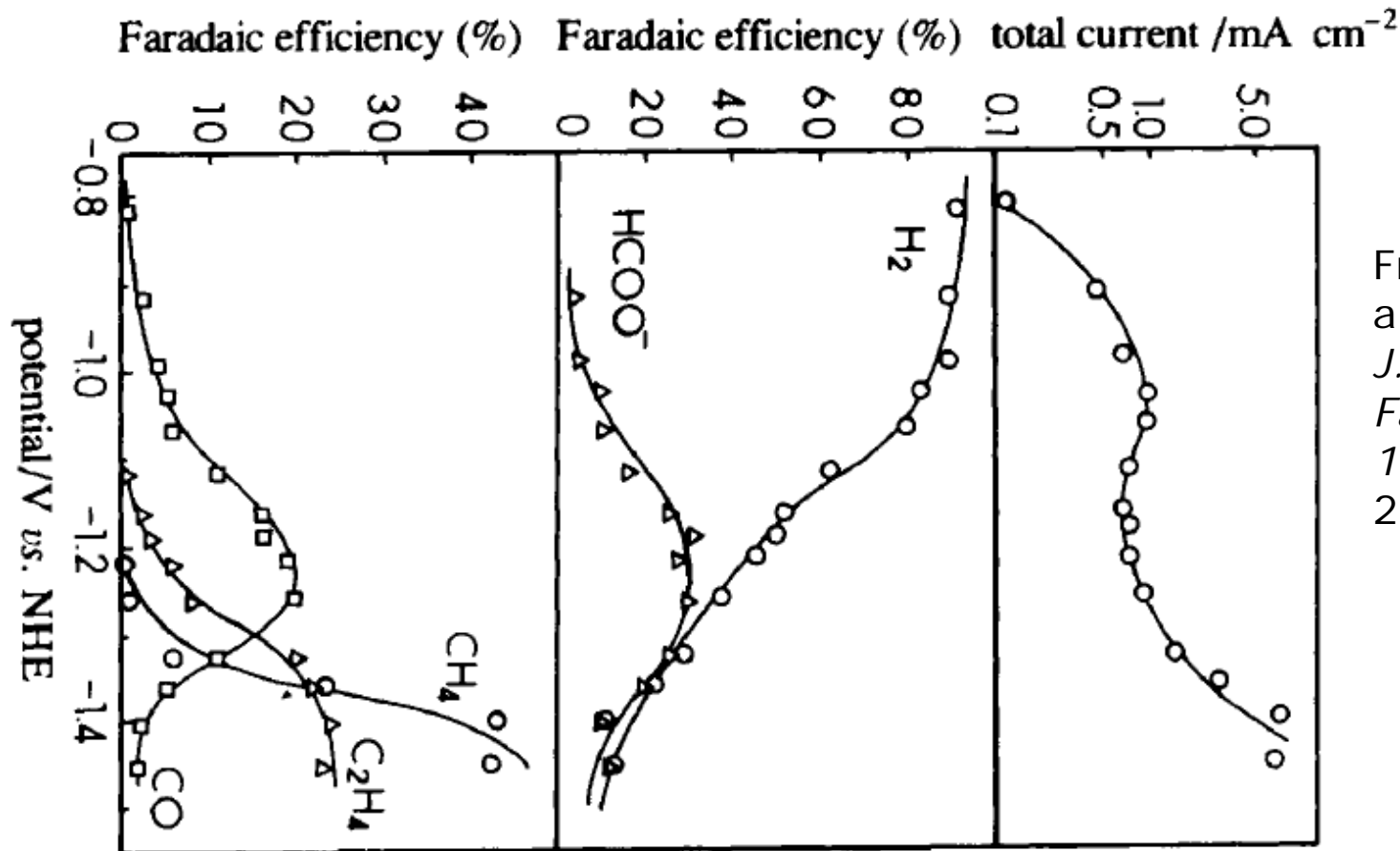
At high current density (above the OH^- limiting diffusion rate) or low pH the OER is reduction of H_2O :



It seems much easier to oxidize OH^- than H_2O or H_3O^+ into O_2

Thus, stay alkaline!

CO₂ reduction at RT and ambient pressure



From Y. Hori et al.,
J. Chem. Soc. Faraday Trans.,
 1, **85** (1989)
 2309

Variation of the Faradaic efficiencies of the products in electrochemical reduction of CO₂, obtained in controlled potential electrolysis, 0.1 mol dm⁻³ KHCO₃, at 19 °C.

Our CO₂ reduction considerations and experience

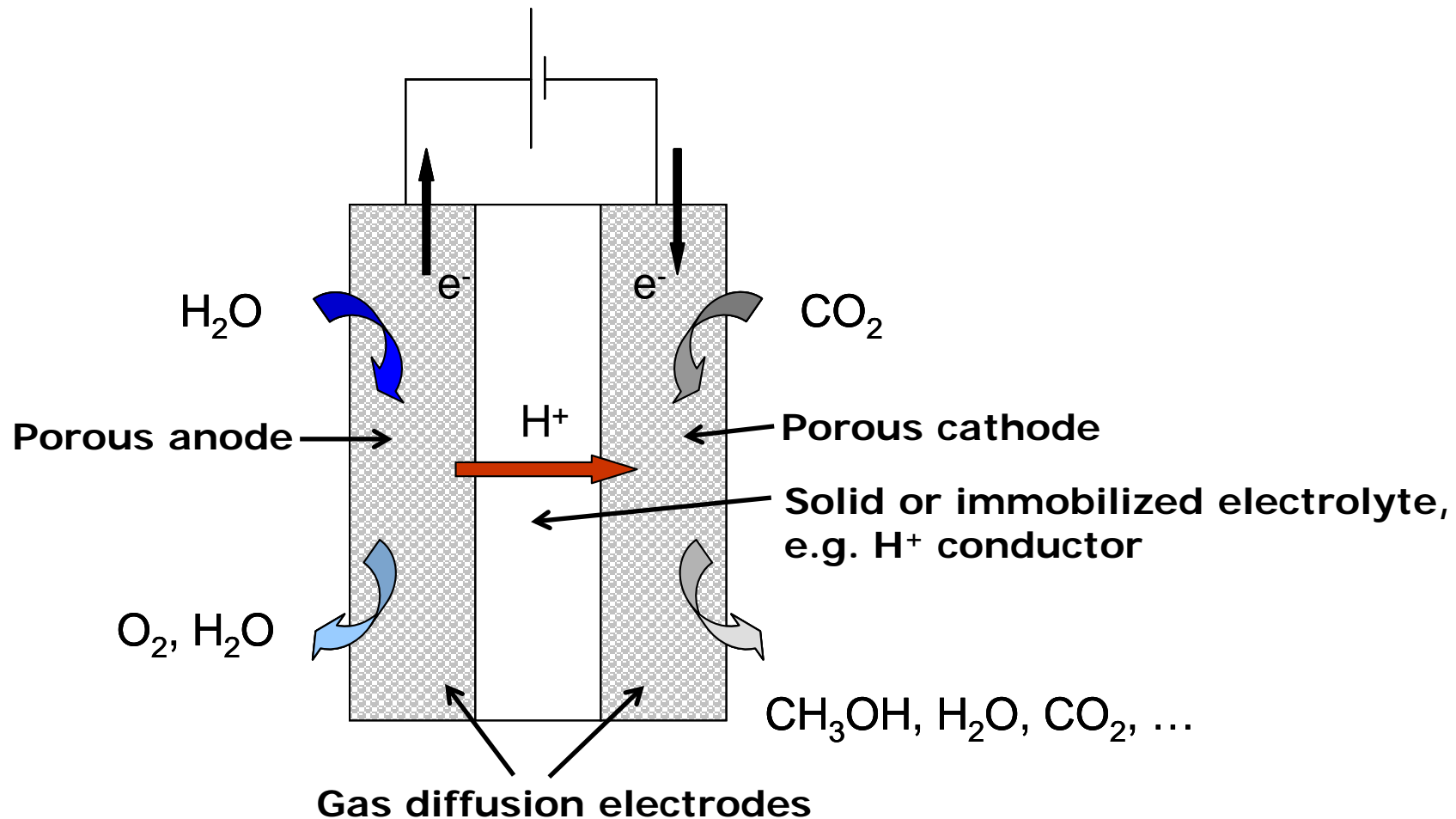


- DTU activities during 4 years aiming at H₂O and CO₂ electrochemical reduction at 200 – 300 °C, pressure up to 50 bar using immobilized aqueous electrolytes and/or solid proton conductor electrolyser cell
- We have 25 years experience in CO₂ and H₂O reduction using SOEC – 750 – 950 °C.
- To have a chance for commercialization CO₂ electrolysis a current density above 1 A cm⁻² at -0.8 to -1.0 V vs NHE and > 80 % yield necessary
- 5 mA cm⁻² at -1.5 V vs NHE and a yield of CH₄ of ca. 45 % is very far from the goal

Why pressurized electrolysis at 200 - 300 °C?

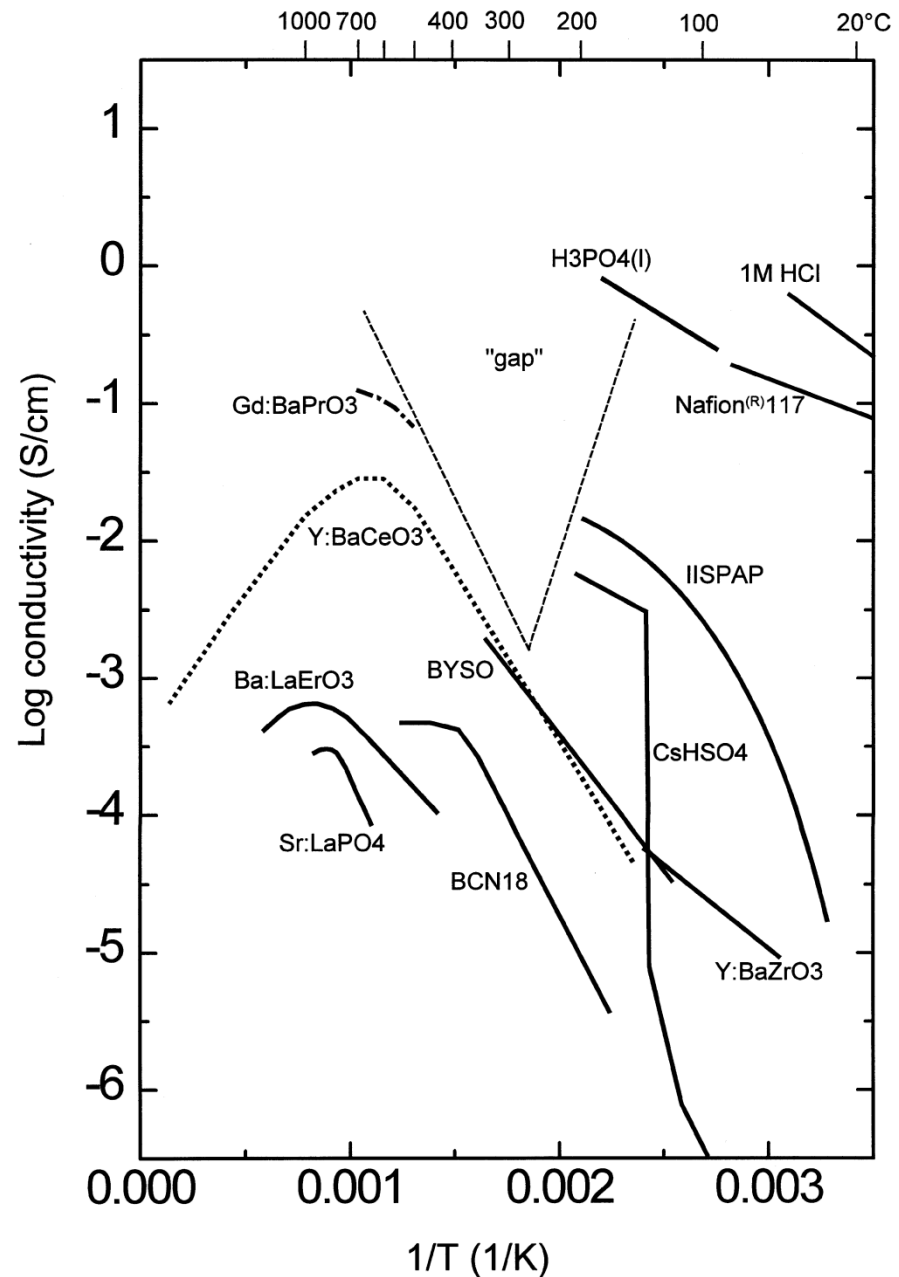
- The electrochemical reaction rate by going from 100 °C to 250 °C and from 1 to 25 bar pressure
- The existing catalyst for conversion of syngas into $C_xH_yO_z$ all operate in this temperature range

Dream cell for 200 – 300 °C



The Norby gap

From T. Norby, *Solid State Ionics*, **125** (1999) 1



Possible “gap closing” electrolytes

- **45 wt% KOH immobilized in ca. 50 % porous ceramics: 0.84 S cm⁻¹ at 200 °C and 25 bar**

F. Allebrod, C. Chatzichristodoulou, P.L. Mollerup, M.B. Mogensen, *Internat. J. Hydrogen Energy*, **37** (2012) 16505, and Proc. of 4th EFCF, paper A0705

- **15 wt% K₂CO₃(aq.): 0.57 S cm⁻¹ at 200 °C measured, ca. 0.3 S cm⁻¹ expected for immobilized electrolyte**

P.L. Mollerup, A.S. Christiansen, N. Bonanos, M.B. Mogensen, submitted for publication 2013

- **Solid acid, CsH₂PO₄: ca. 10⁻² S cm⁻¹ at 240 °C (“the limit”).**

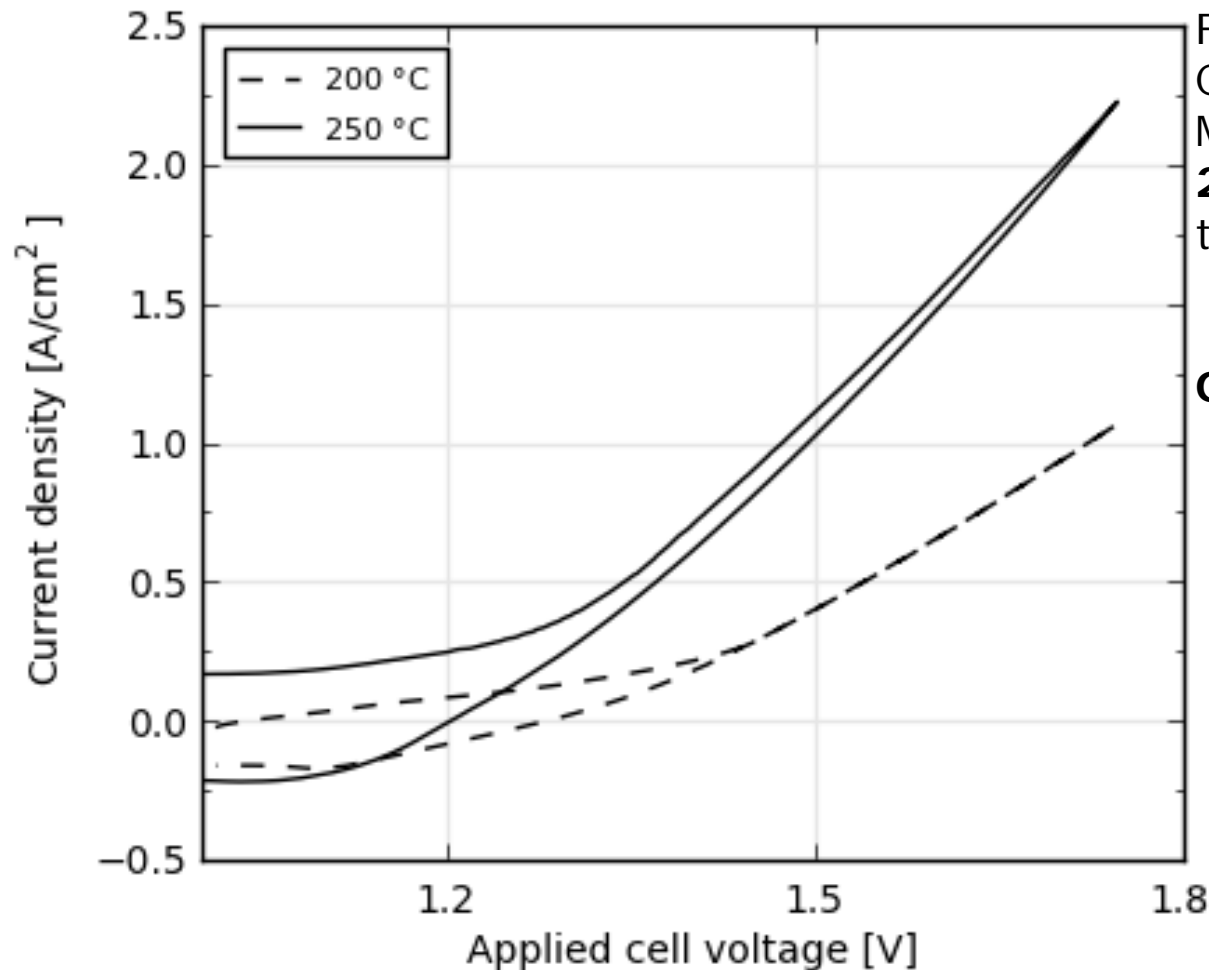
S.M. Haile, C.R.I. Chisholm, K. Sasaki, D.A. Boysen, T. Uda, Solid acid proton conductors: from laboratory curiosities to fuel cell electrolytes, *Faraday Discussions*, **134** (2007) 17

- **Acceptor doped metal phosphorous oxides such as Ce(PO₃)₄ and CeP₂O₇ - high initial conductivity – not stable over time > 100 h**

C. Chatzichristodoulou, J. Hallinder, A. Lapina, P. Holtappels, M. Mogensen, *J. Electrochem. Soc.*, **160** (2013) F1

- **BaCe_xZr_yY_zO_{3-d} might be possible at 300 °C if its grain boundary resistance could be reduced – it can by adding ceria, which makes the material degrade fast in CO₂, so.... ?**

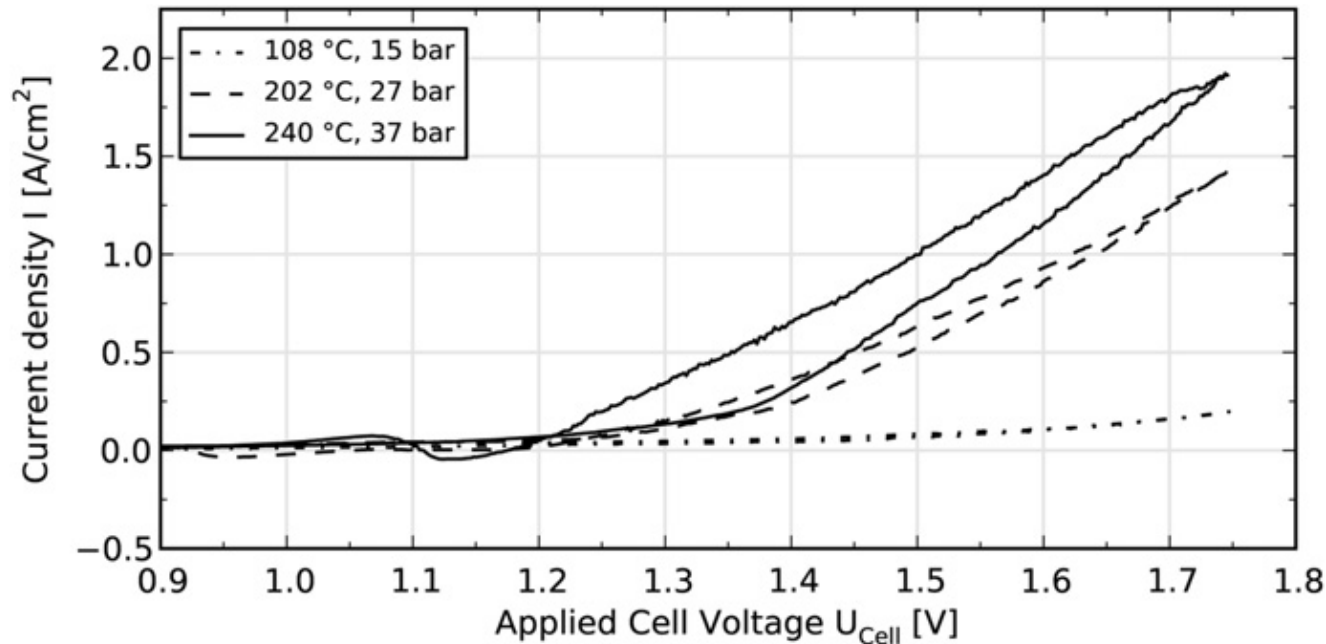
Performance of cells with immobilized KOH(aq.) at 40 bar



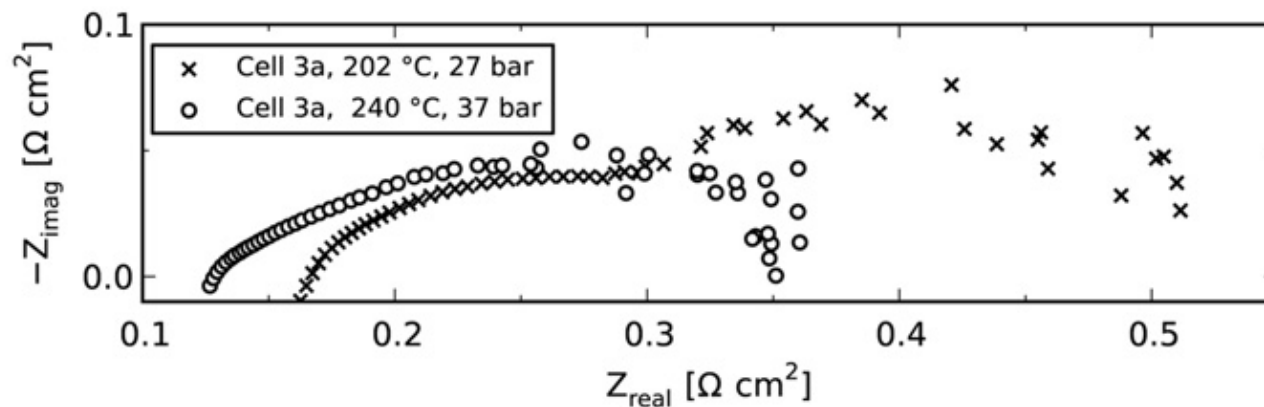
F. Allebrod, C. Chatzichristodoulou, M.B. Mogensen, *J. Power Sources*, **229** (2013) 22, and in Proc. of this meeting, paper A0705.

Only H₂

Effect of Temperature, Alkaline Electrolysis

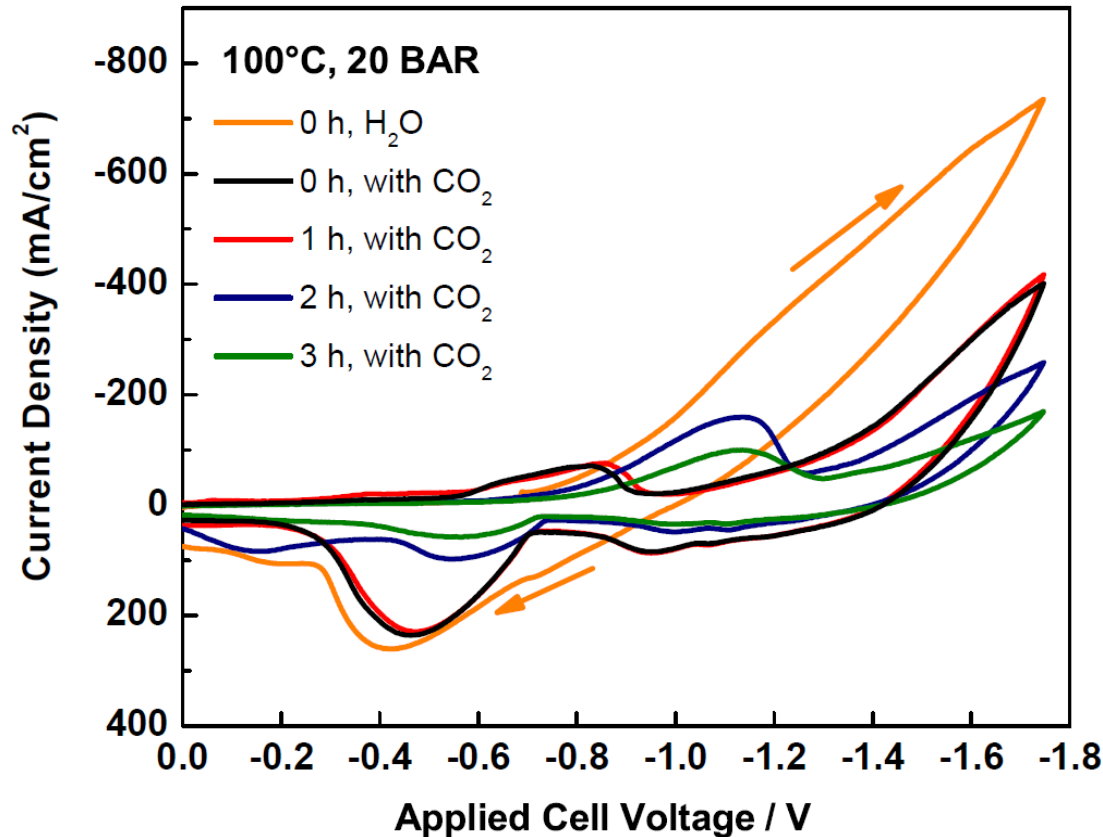


Cells with 45 wt% KOH (aq.) immobilized in mesoporous ceramic membrane (electrolyte) and with gas diffusion electrodes. Cathode: Inconel. Anode Ag deposited on Ni.



From: Allebrod, Chatzichristodoulou, Mogensen, J. Power Sources **229** (2013) 22

Effect of carbonates in KOH(aq.) cells

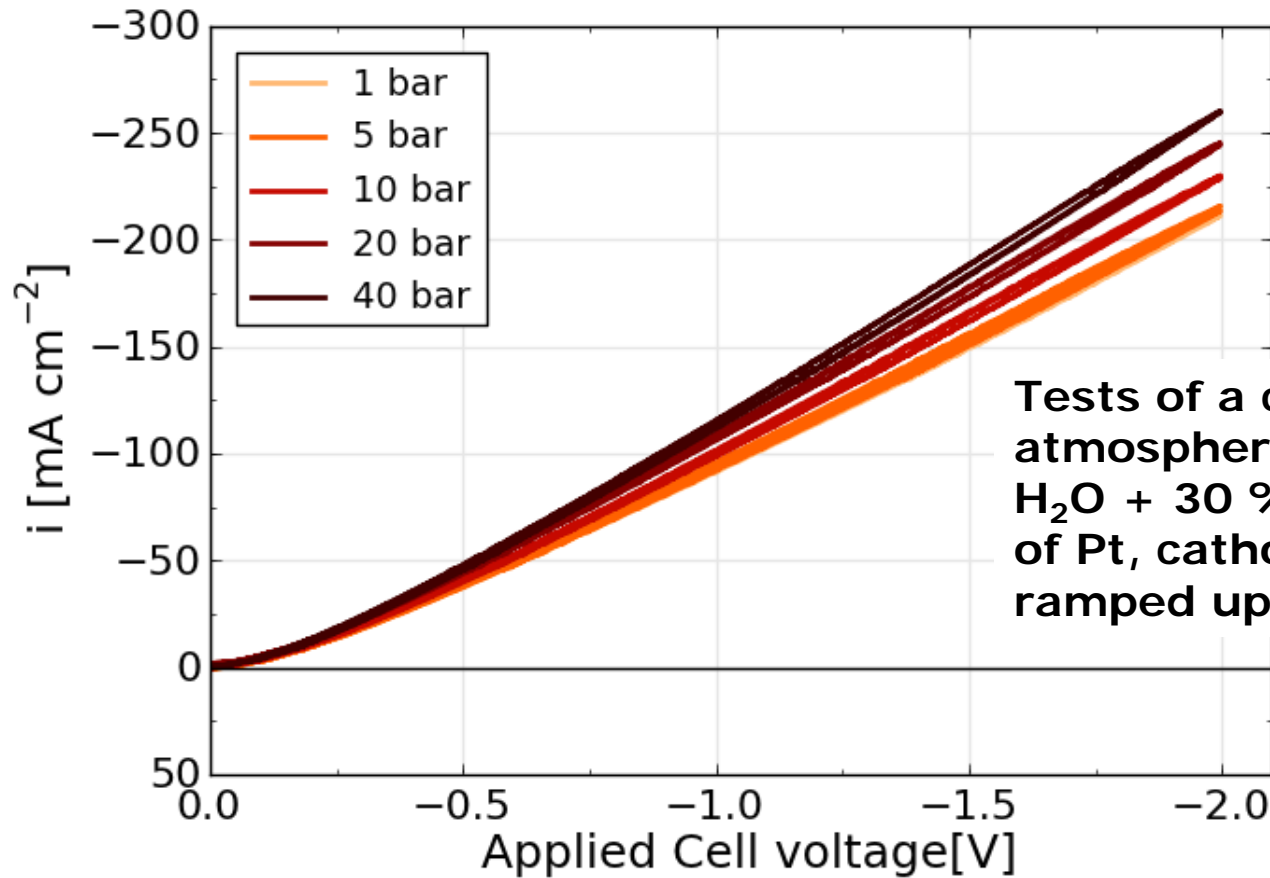


Addition of CO₂ gas to a cell with KOH(aq.) immobilized electrolyte.

Gas flow to anode side: H₂O [25 sccm] / N₂ [375 scm³] / H₂ [5 sccm] and cathode side: CO₂ [10 sccm]).

CO₂ slows down the electrode kinetics very much almost immediately.

CsH_2PO_4 solid acid cell



Only H_2

CO_2 tested – no CO

Tests of a cell in single atmosphere of 50 % H_2 + 20 % H_2O + 30 % N_2 . $T = 240^\circ\text{C}$, anode of Pt, cathode of Cu. Pressure was ramped up from 1 to 40 bar

Molten carbonate electrolyser cell - I

- **Recent break-through electrolysis of CO₂ into CO using molten carbonate electrolytes** (V. Kaplan, E. Wachtel, K. Gartsman, Y. Feldman, I. Lubomirsky, *J. Electrochem. Soc.*, **157**, (2010) B552; S. Licht, *Advanced Materials*, DOI: 10.1002/adma.201103198)
- **Cell types used for molten carbonate fuel cells not usable for electrolysis**
- **Pure molten Li₂CO₃ above 800 °C has shown feasible as electrolyte, Ti-Al-metal alloy as cathode (CO evolution) and graphite as anode (O₂ evolution)**
- **Chemical equilibrium of CO₃²⁻ ⇌ CO₂ + O²⁻ is assumed**
- **CO₂(l) + 2 e⁻ → CO(l) + O²⁻(l)**
- **O²⁻(l) → ½ O₂(l) + 2 e⁻**

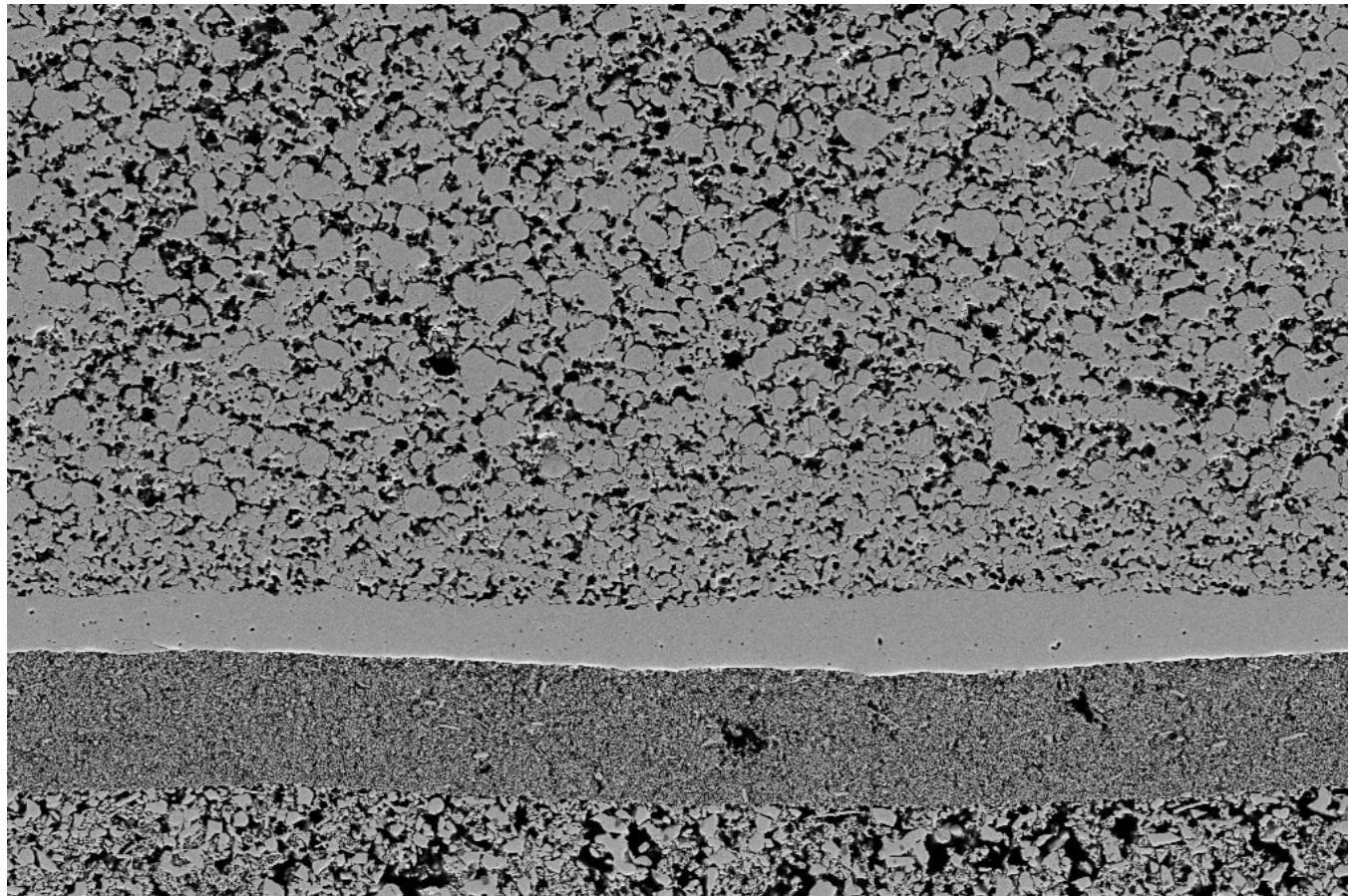
Molten carbonate electrolyser cell - II

- CO and O₂ very little soluble in molten Li₂CO₃ and they escape into gas phase separately:



- Pure CO rather than a mixture of CO and CO₂ is produced in contrast to the other two CO₂ electrolysis cells.
- Relatively fast electrode kinetics of ca. 1 A cm⁻² at 1.5 V overvoltage due to the high temperature of 900 °C

Ni-YSZ supported SOC



Ni/YSZ support

Ni/YSZ electrode
YSZ electrolyte

LSM-YSZ electrode



10 μm

EHT = 12.00 kV

Signal A = SE2

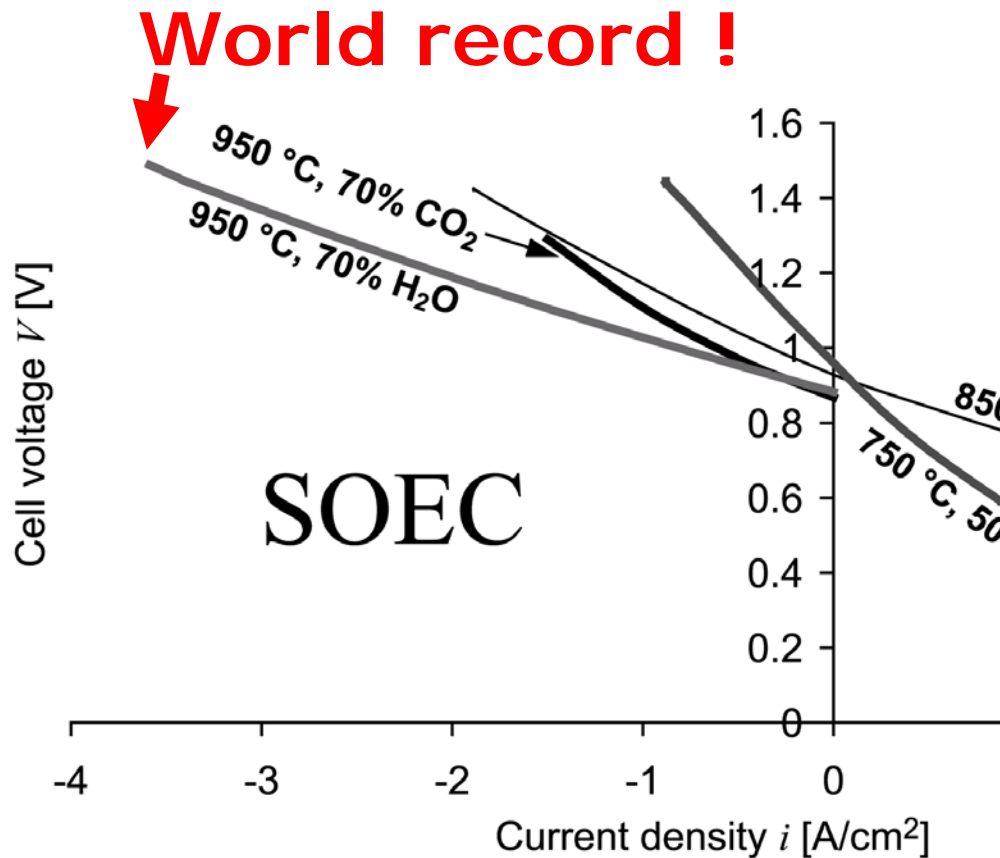
Date : 18 Jan 2006

Acc. voltage: 12 kV

SE image



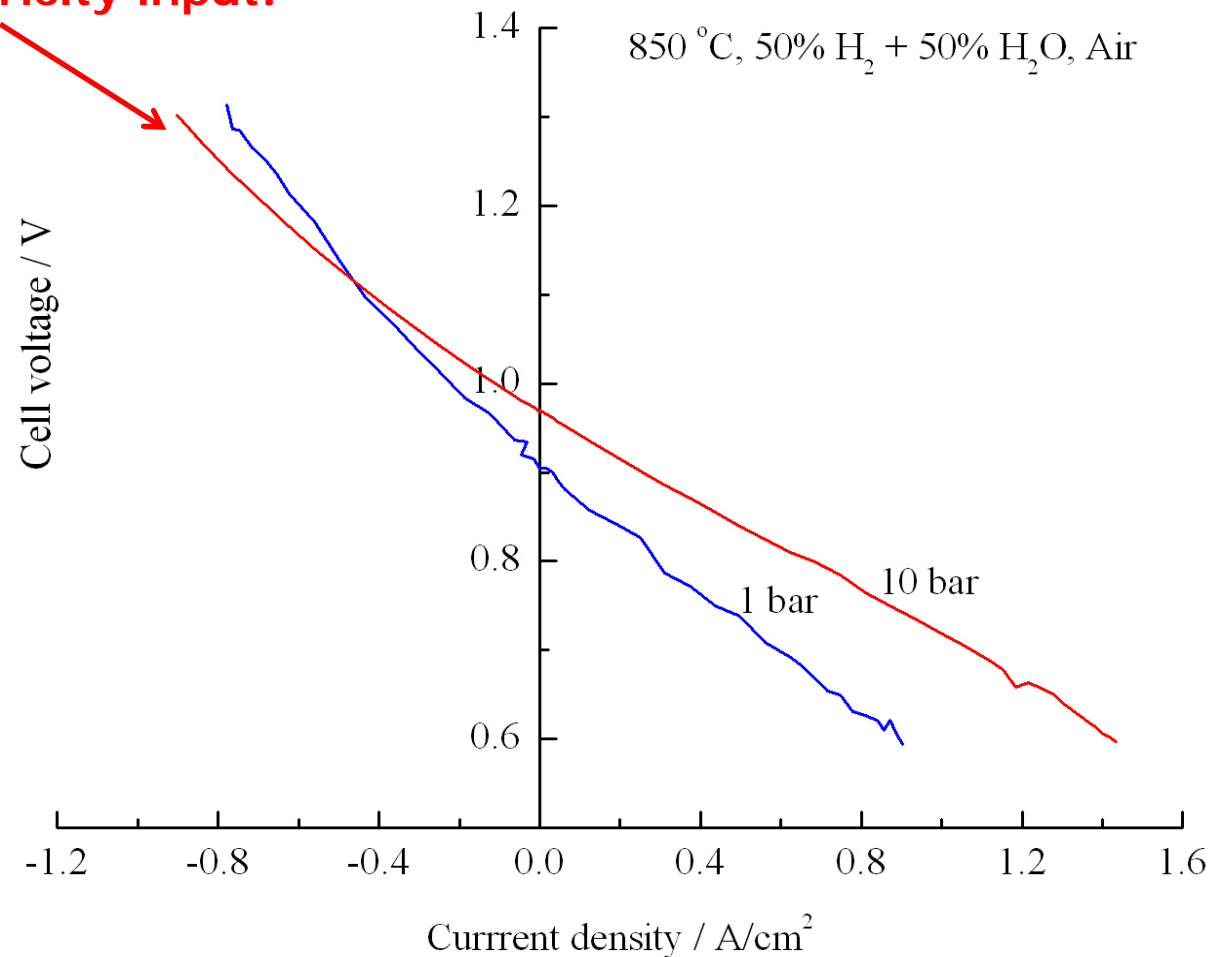
SOEC Cell performance



i - V curves for a Ni-YSZ-supported Ni/YSZ/LSM SOEC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO₂ partial pressures - balance is H₂ or CO. S.H. Jensen et al., International Journal of Hydrogen Energy, **32 (2007) 3253**

SOEC Effect of pressure

We get pressurized hydrogen with lower electricity input!



SOC is being improved significantly

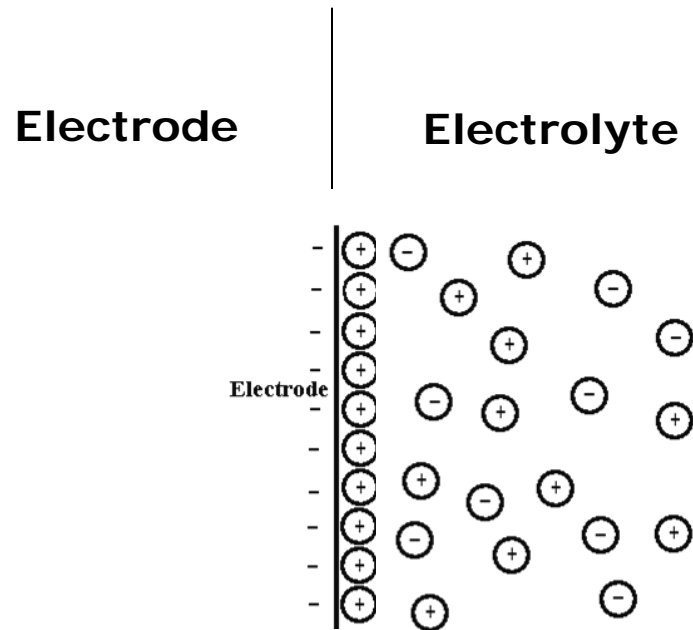
- The above results were from “old fashion” SOC with LSM electrodes and 10 micron electrolyte with ASR of $0.22 \Omega \text{ cm}^2$ at 850°C
- Much improved cells have been reported since, see literature from FZ-Jülich, KIT, DTU Risø, The Wachsman group in US, e.g. the FZ-J/KIT paper: F. Han et al., J. Power Sources, 218 (2012) 157. Their best cell was about $0.1 \Omega \text{ cm}^2$ at 750°C in electrolyser mode
- These super results have yet to be implemented in stacks and tests also in electrolysis mode

Kinetic models

Fundamental question: To which extent is the classical double layer electrode model and Butler-Volmer kinetics describing electrode kinetics in electrochemistry for energy conversion – and in particular in solid state electrochemistry?

Is simple charge transfer across a well-defined potential barrier the kinetic barrier of practical electrodes such as those of SOC and other electrochemical cells for energy purposes?

Double layer at electrodes in aqueous electrolytes



This is the simplified picture for a metal electrode in a liquid electrolyte.

In real systems the interface is not atomically flat. There will at least be roughness with vacancies, steps and kinks on the surface, where the reactions tend to take place.

Segregation to YSZ surfaces

Surface	
Impurity layer	~ 0.5 nm
Layer enriched in Y_2O_3	~ 5 - 10 nm
Bulk phase YSZ	
a)	

Surface	
Impurity layer	~ 0.5 nm
Layer enriched in Y_2O_3	~ 1 nm
Layer depleted in Y_2O_3	~ 5 nm
Bulk phase YSZ	
b)	

YSZ with glassy surface layers of SiO_2 , Na_2O , CaO + + +.

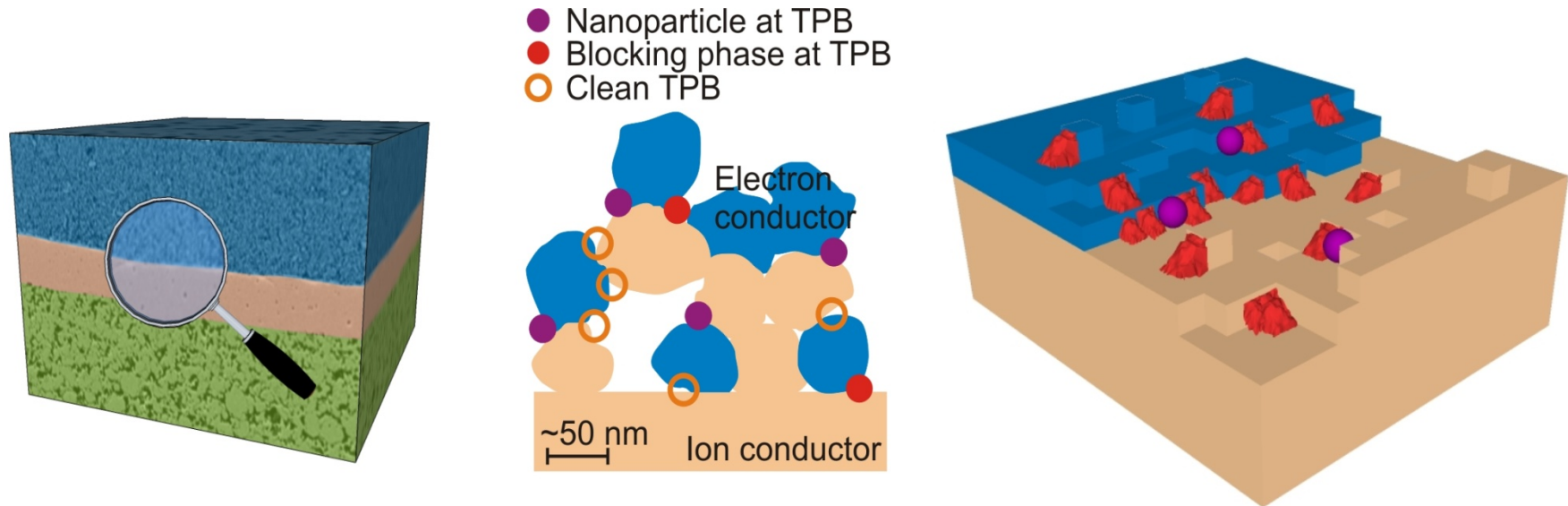
a) Near equilibrium ($> 1200\text{ }^\circ\text{C}$) several hours

b) Not near equilibrium - the original surface removed +1 h at $500\text{ }^\circ\text{C}$.

- The exact YSZ surface depend on initial composition and on sample history
- Similar segregations on perovskite surfaces, i.e. ceramic electrodes – for instance Sr enrichment on LSM and LSCo surfaces

M. Mogensen, K.V. Hansen, in: Handbook of Fuel Cells, 2009.

SOC electrode structure



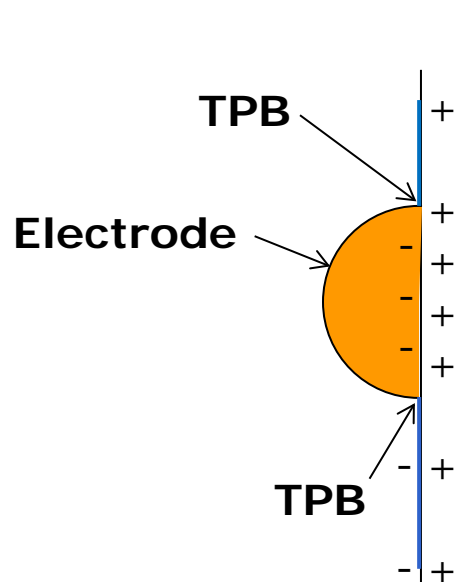
Solid oxide cell and the oxygen electrode.

Left: cell structure with 3 thin ($10 - 80 \mu\text{m}$) layers: fuel electrode (green), electrolyte (beige) and oxygen electrode (blue).

Middle: magnification of composite oxygen electrode.

Right: 3-D picture of how TPB may look on atomic scale. Many different surface sites are possible electrocatalytic active sites.

Space charges in solid state?



Electrolyte

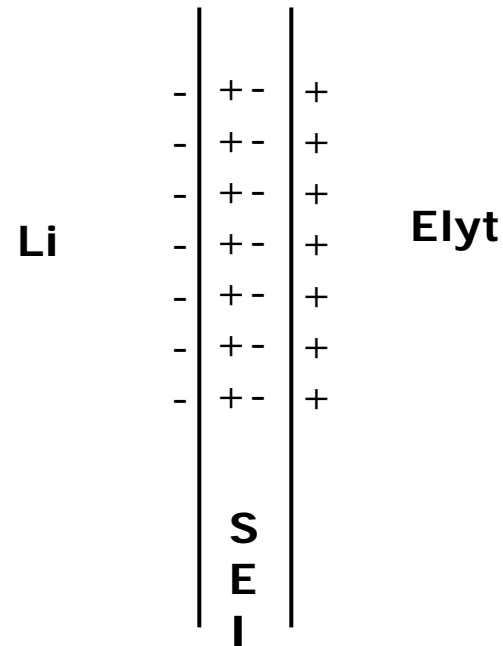
In e.g. YSZ “+” is equivalent to an oxygen vacancy

This means another composition and in some cases new phases.

Also along grain boundaries space charge is also accumulated

This is also a very simplified picture of the double layer and space charge distribution.

Space charges in/on a Li electrode



Some concluding recommendations

- Liquid electrochemistry not feasible to describe SOC or Li-battery electrochemistry
- SOC and many other interfaces are very sensitive to history in general and thermal history in particular and so is electrochemistry - difficult to make equal cells in different institutes /companies
- Thus, searching for one universal rate limiting reaction step for a given type of SOC composite electrode may not be very useful
- Instead the study of various structures and of which physical and chemical properties of solids that give best electrocatalytic activity is recommended (TPB structure very important in SOC – use of 3D FIB-SEM, TEM and in-situ surface analysis, Raman, CAHT-SPM, + + +
- Furthermore, better three-dimensional micro-models describing charge transport to and from the electrodes are needed

Acknowledgements

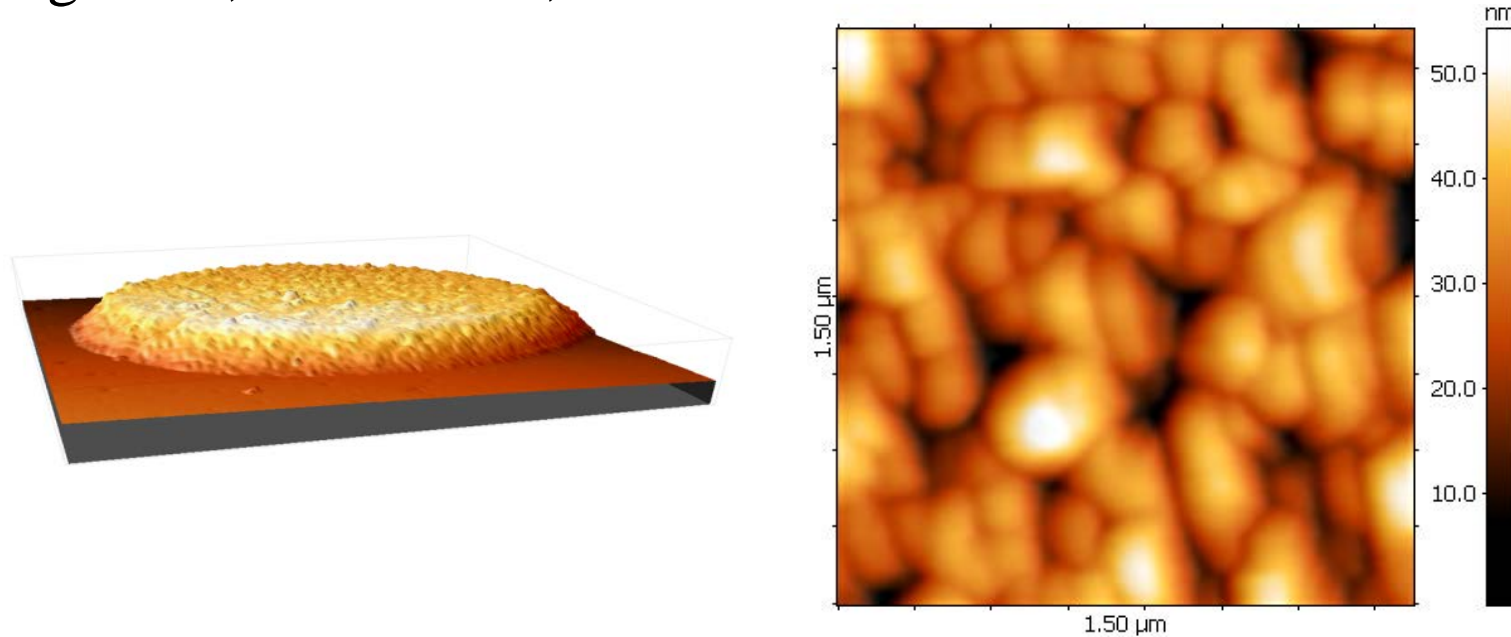
I acknowledge support from our sponsors

- Danish Energy Authority  **DANISH ENERGY AUTHORITY**
- Energinet.dk 
- EU 
- Topsoe Fuel Cell A/S 
clean, efficient and reliable
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
- The work of many colleagues over the years

Thank you for your attention

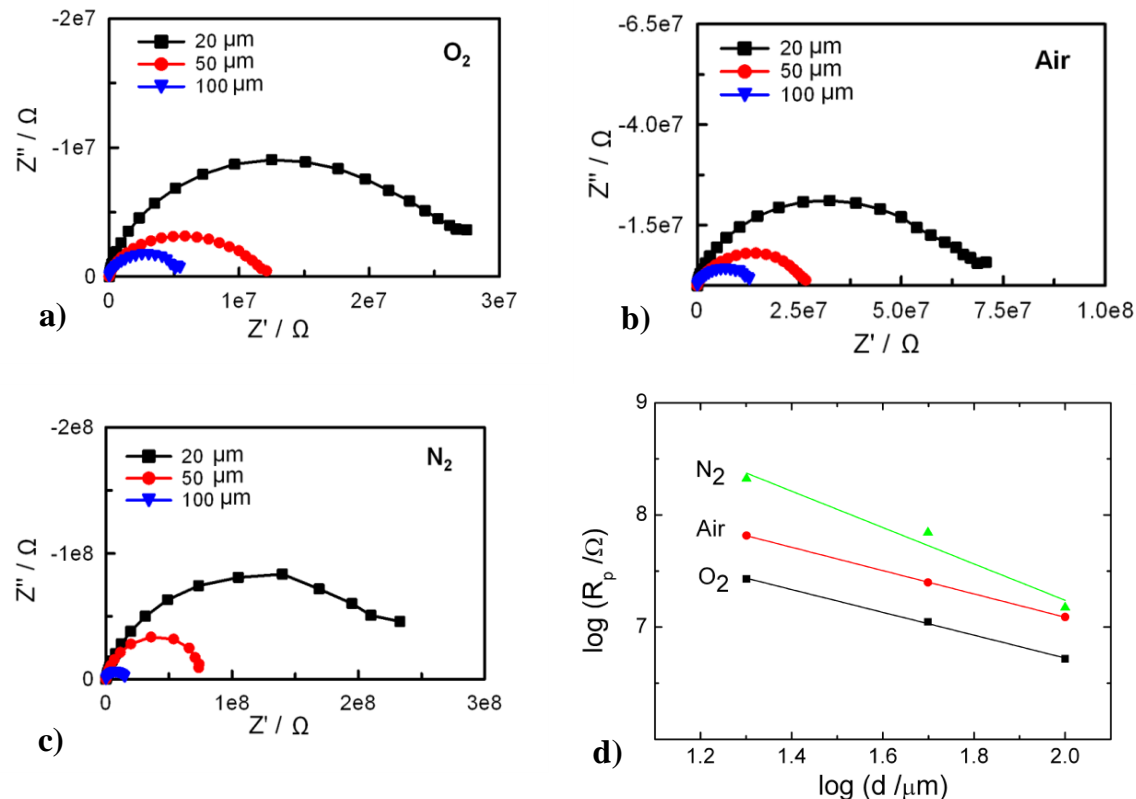
Electrode kinetics – LSM microelectrodes

Y. Wu, K. V. Hansen, K. Norrman, T. Jacobsen, M.B. Mogensen, SOFC XIII, Oct. 2013



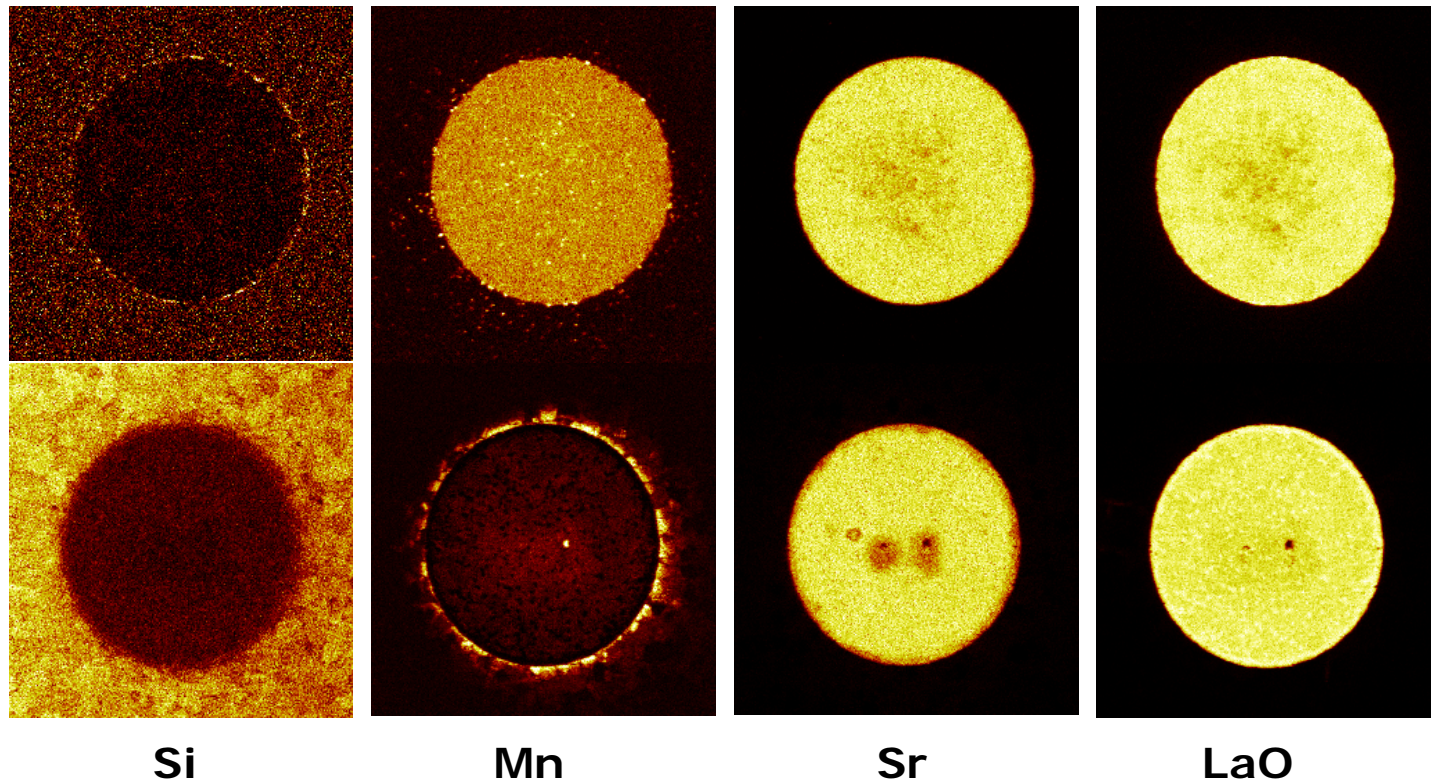
AFM images showing overview (left) and surface morphology (right) of a 50 μm diameter and 0.5 μm thick LSM microelectrode.

EIS using CAHT-SPM - Size variation



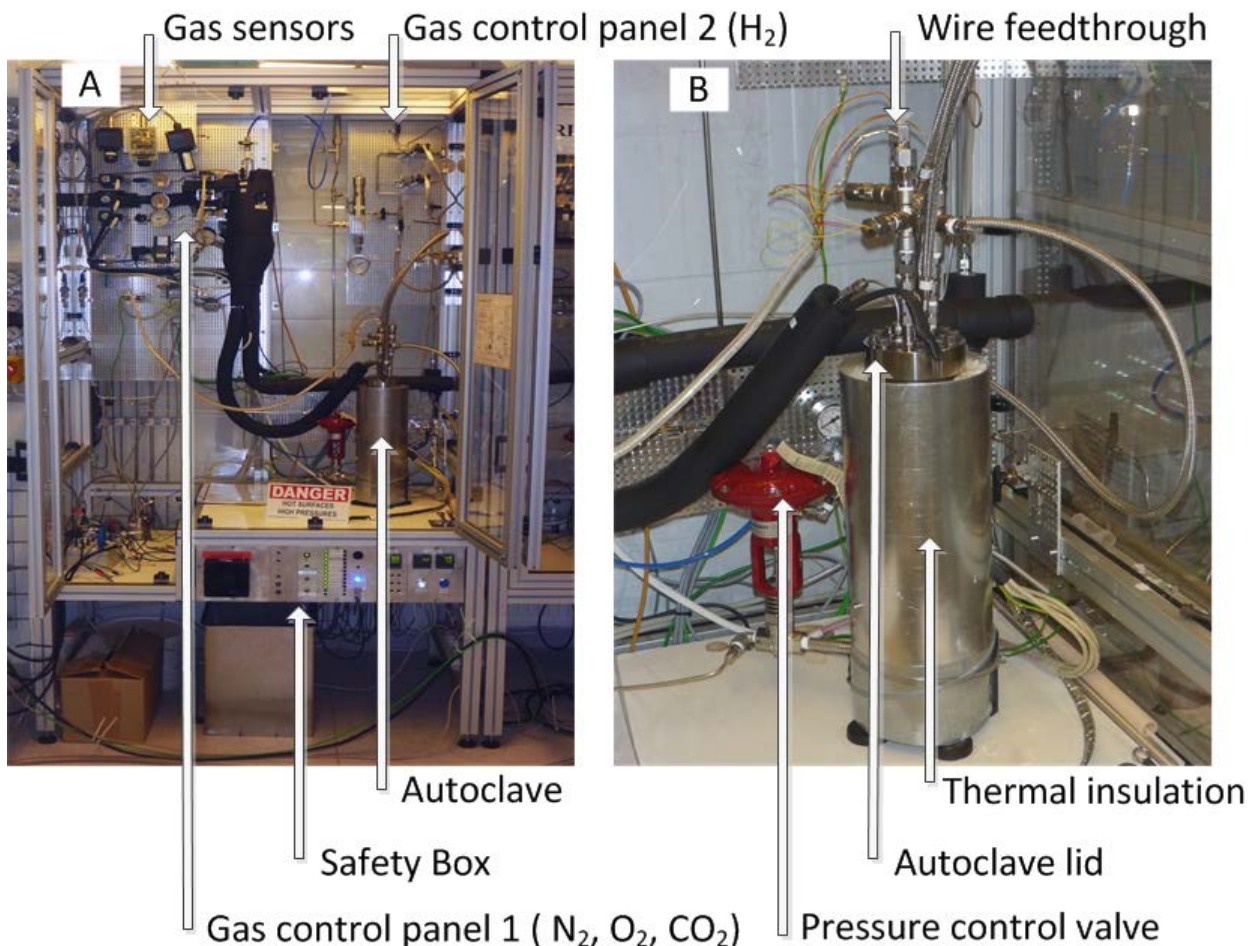
Impedance spectra of LSM microelectrodes measured at OCV at $856^\circ C$ in a) pure oxygen, b) air and c) N_2 , and d) a double-logarithmic plot of the electrode polarization resistance (R_p) versus the microelectrode diameter, d , derived from the shown impedance spectra. The slopes obtained by linear regression are -1.02 ± 0.04 , -1.04 ± 0.00 , and -1.62 ± 0.28 in pure O_2 , air and N_2 ($pO_2 \approx 10^{-4}$ bar), respectively.

Surface composition



TOF-SIMS of two 100 μm microelectrodes, a not tested reference (upper row) and an electrochemical tested (lower row) for the 4 signals from Si, Mn, Sr and LaO. The lighter, the higher is the signal (the counts) of a given species

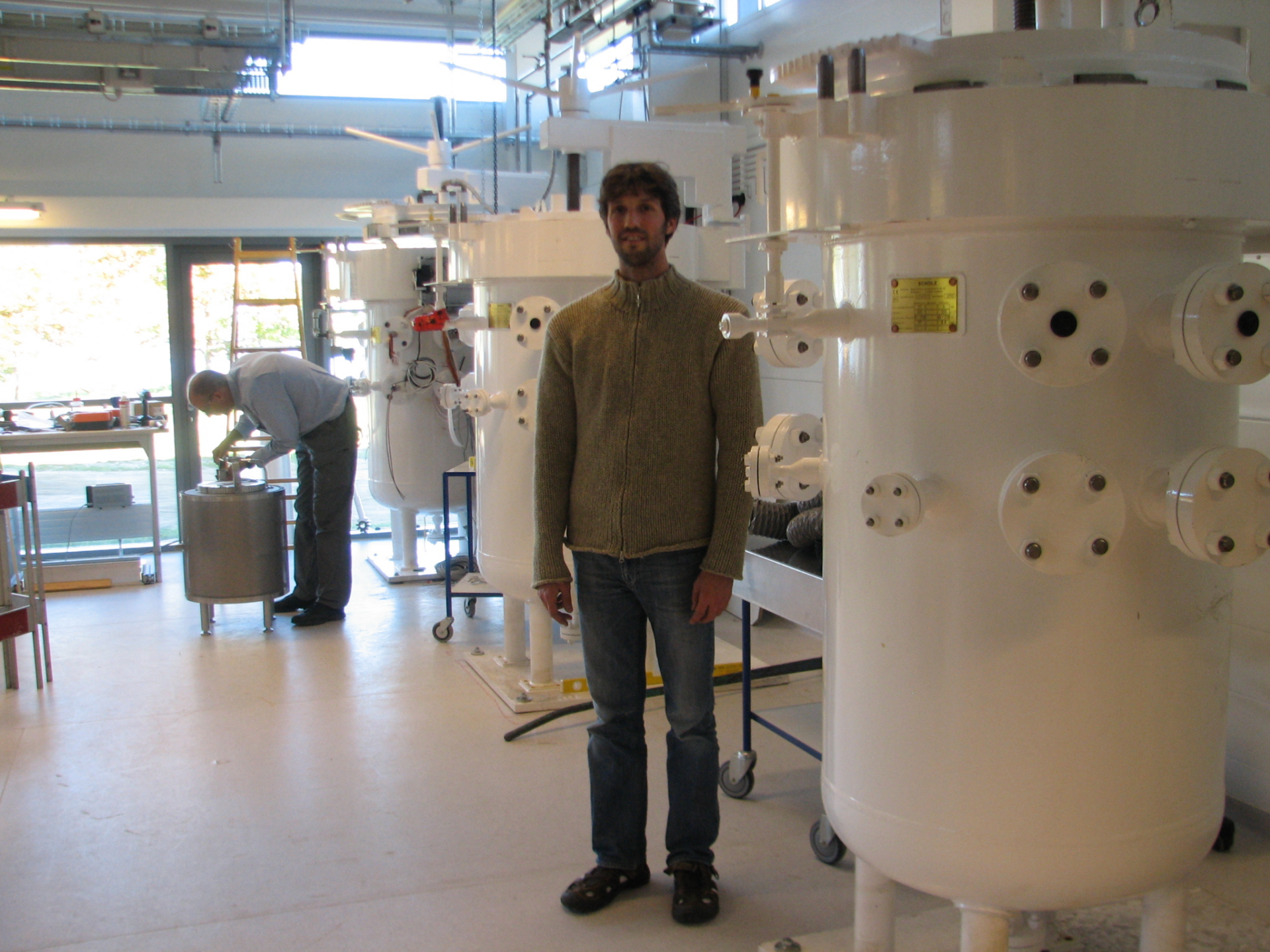
5 fully automatized high temperature and pressure setups – 3 are operational now



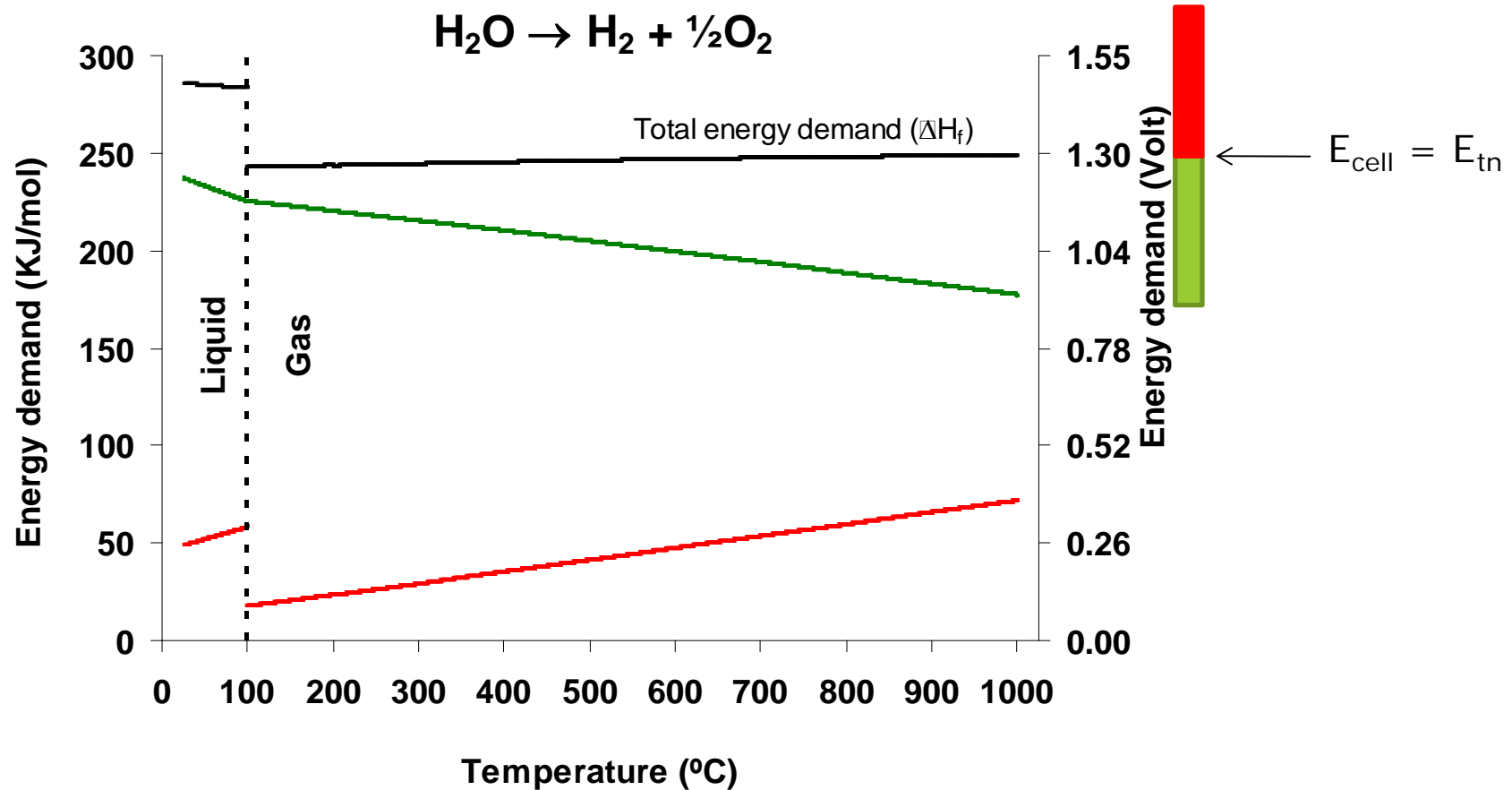
Specifications

Producer	Custom
Vessel material	Inconel 625, Steel
Volume	500 ml
P_{max}	95 bar
T_{max}	300 °C
Liner material	Ti, PTFE
$T_{max, PTFE}$	250 °C

C. Chatzichristodoulou, F. Allebrod, and M. Mogensen. High temperature and pressure electrochemical test station. *Review of Scientific Instruments*, 84(5):054101-054112



Thermodynamics



$$\text{Energy ("volt")} = \text{Energy (kJ/mol)} / 2F$$

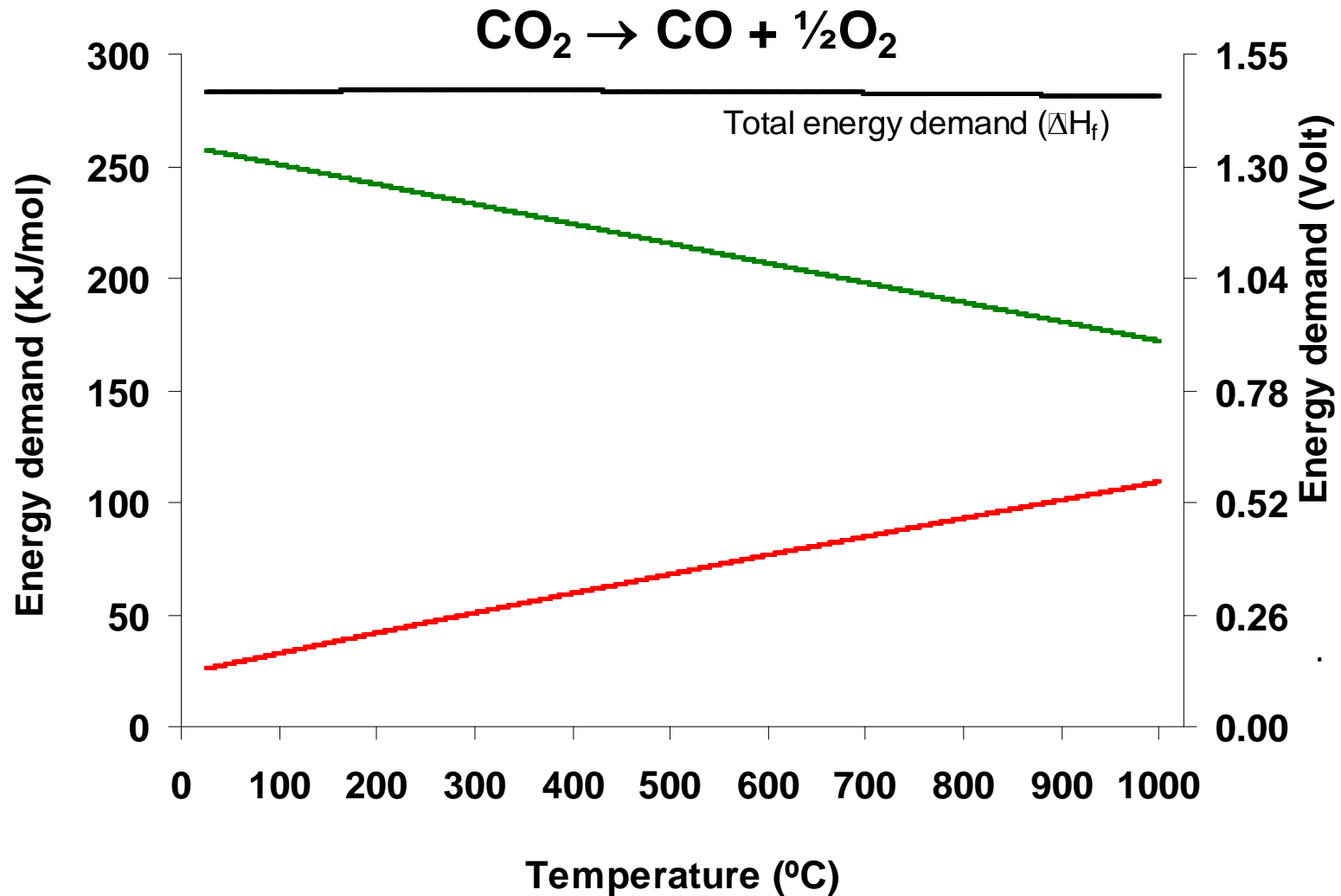
$$i \propto E_{\text{cell}} - \Delta G / 2F$$

$$E_{\text{tn}} = \Delta H / 2F$$

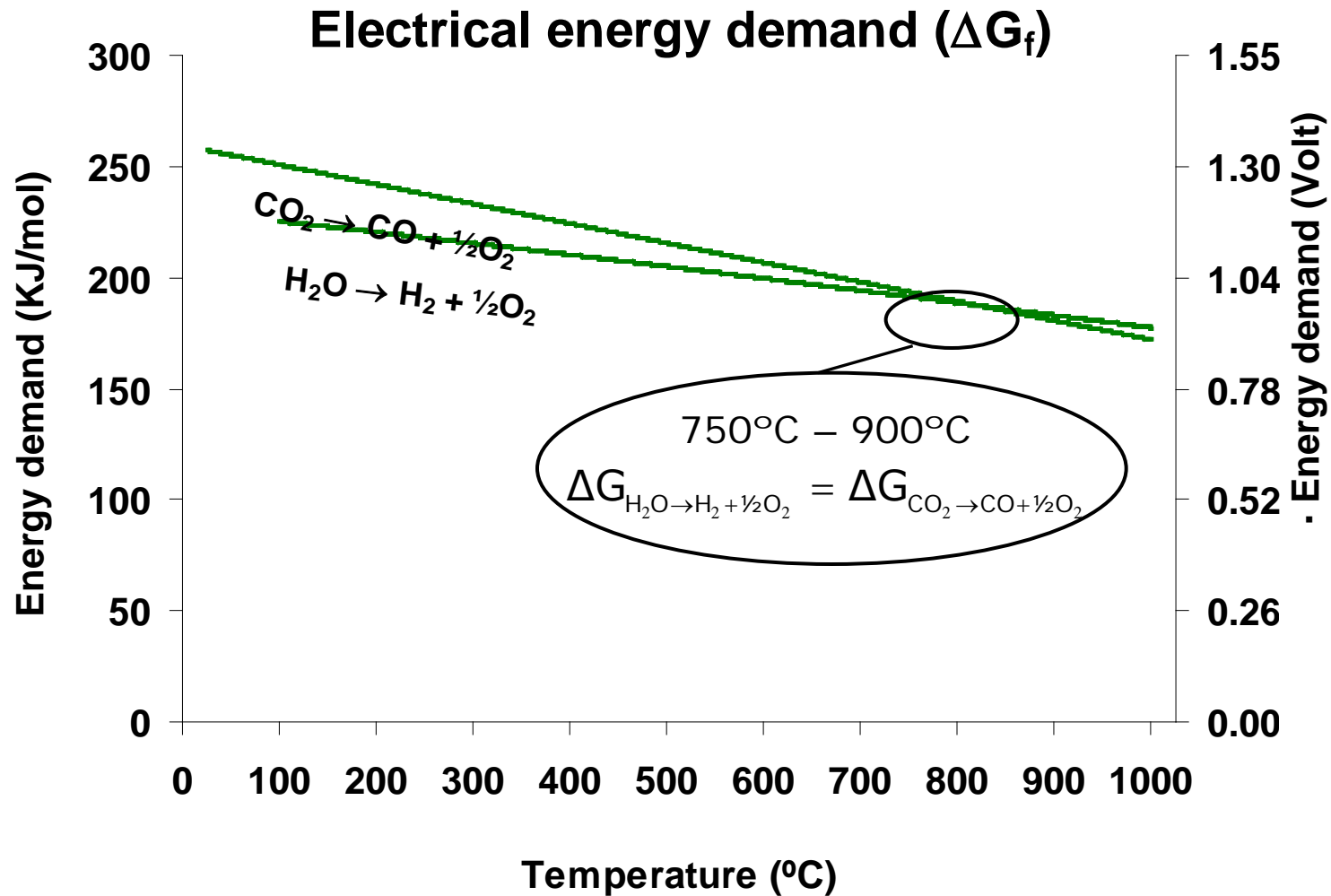
$$\text{Price} \propto 1/i \quad [\text{A/cm}^2],$$

$$\Delta H / \Delta G > 1, \quad \eta = 100 \% \text{ at } E = E_{\text{tn}} \text{ (no heat loss)}$$

Thermodynamics



Thermodynamics: CO₂ and H₂O



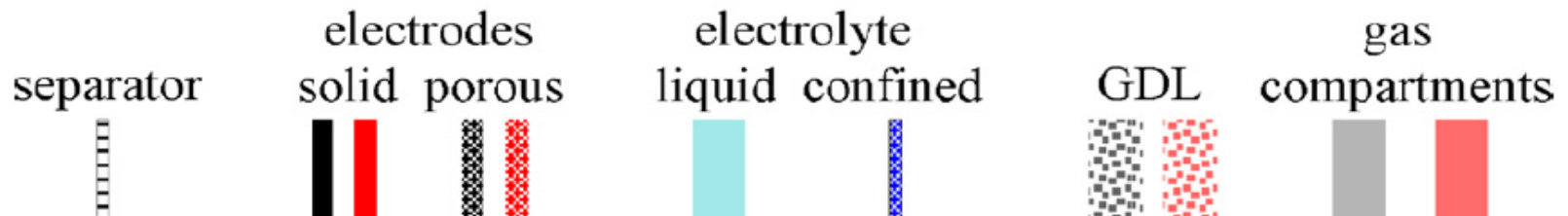
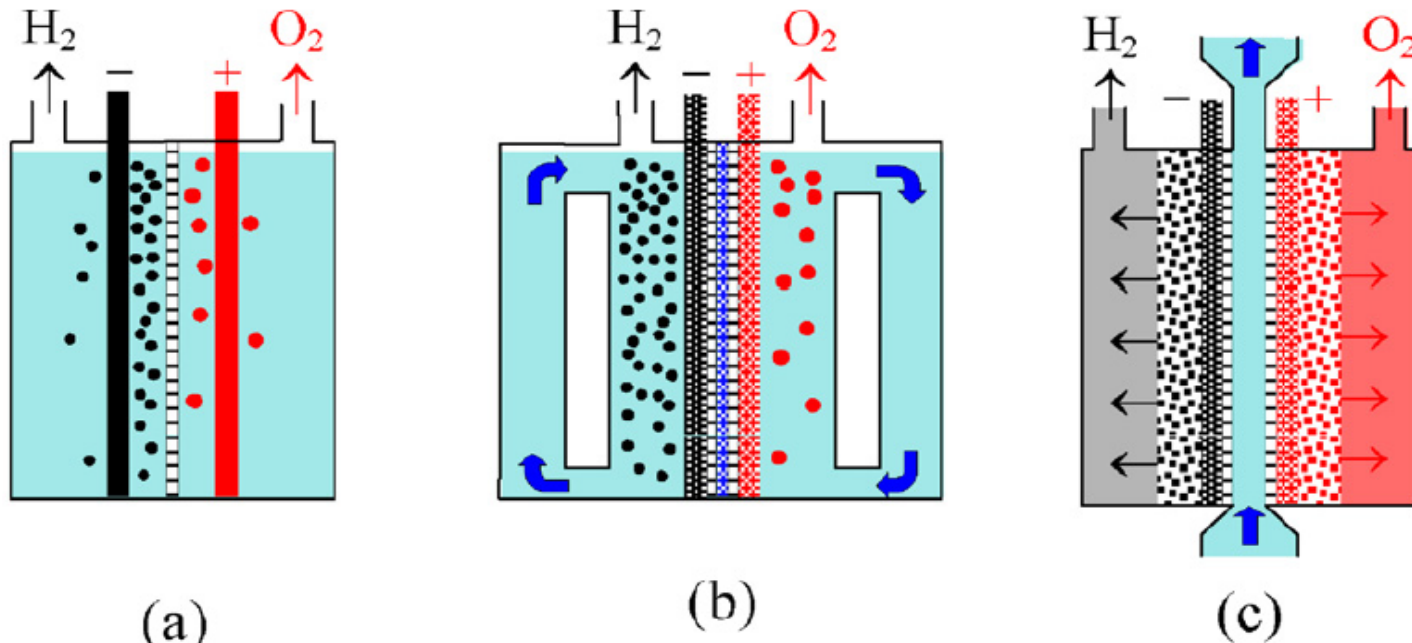
Why synthetic hydrocarbons?

The energy density argument

Comparison of Energy Storage Types. Only the batteries are including containers.

Storage type	MJ/L	MJ/kg	Boiling point, °C
Gasoline	33	46	40 – 200
Dimethyl ether - DME	22	30	- 25
Liquid methane	24	56	-162
Liquid hydrogen	10	141	-253
Compressed air – 20 MPa	0.1	0.4	
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

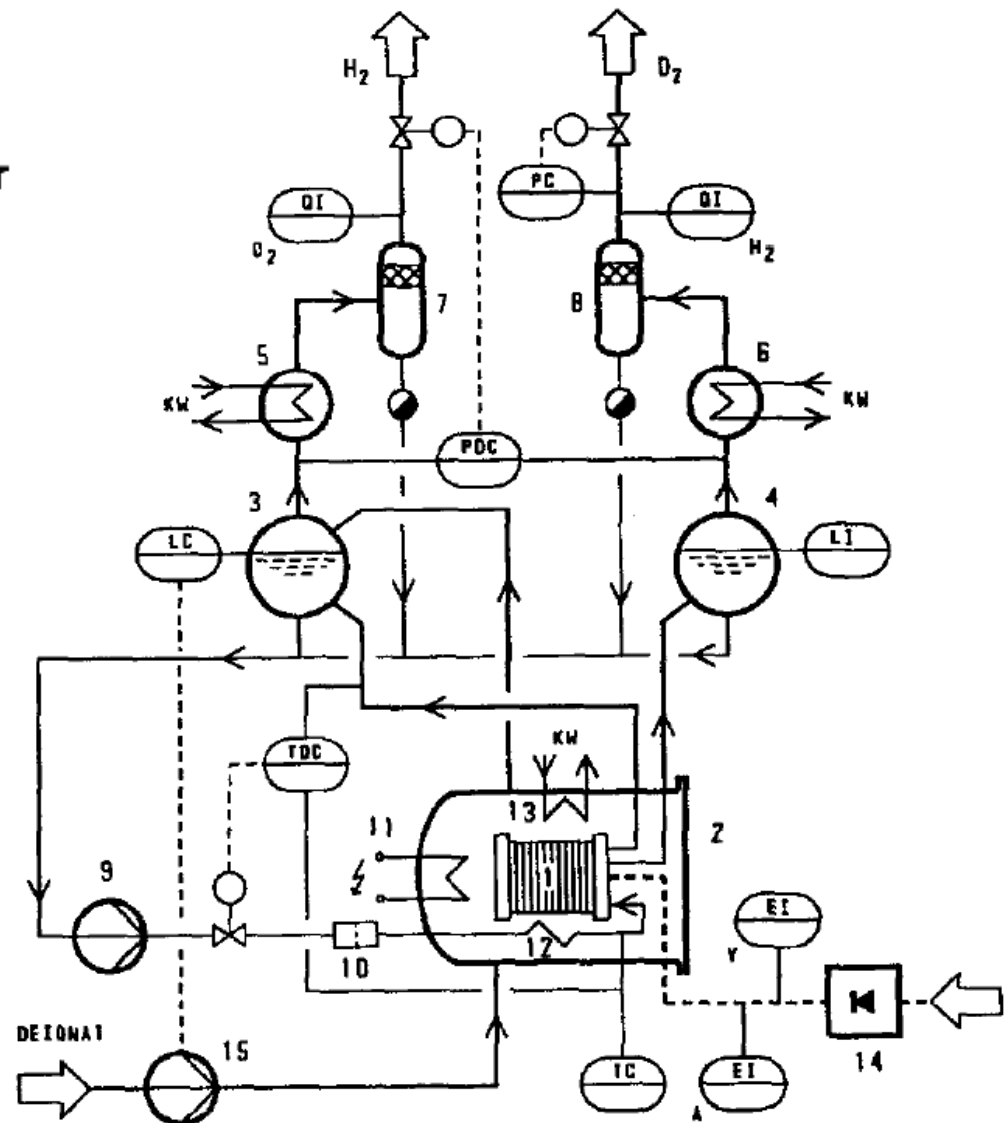
Principle designs



Different architectures of electrolyzers with: (a) immersion electrodes, (b) porous electrodes in the "zero-gap" configuration, (c) electrodes comprising Gas Diffusion Layers (GDL) separating the gas compartments and the recirculating electrolyte compartment. From: S. Marini et al., *Electrochimica Acta*, **82** (2012) 384

Process flow diagram of a modern electrolyzer

- 1 Electrolytic cells
- 2 Electrolyzer pressure vessel
- 3 Hydrogen-electrolyte separator
- 4 Oxygen-electrolyte separator
- 5 Hydrogen cooler
- 6 Oxygen cooler
- 7 / 8 Condensate separators
- 9 Electrolyte circulating pump
- 10 Electrolyte filter
- 11 Electric heater
- 12 Electrolyte heater/cooler
- 13 Water cooler
- 14 Rectifier unit
- 15 Electrolyte feed pump



In principle reversible,
but not in practice

Hydrogenics Alkaline system

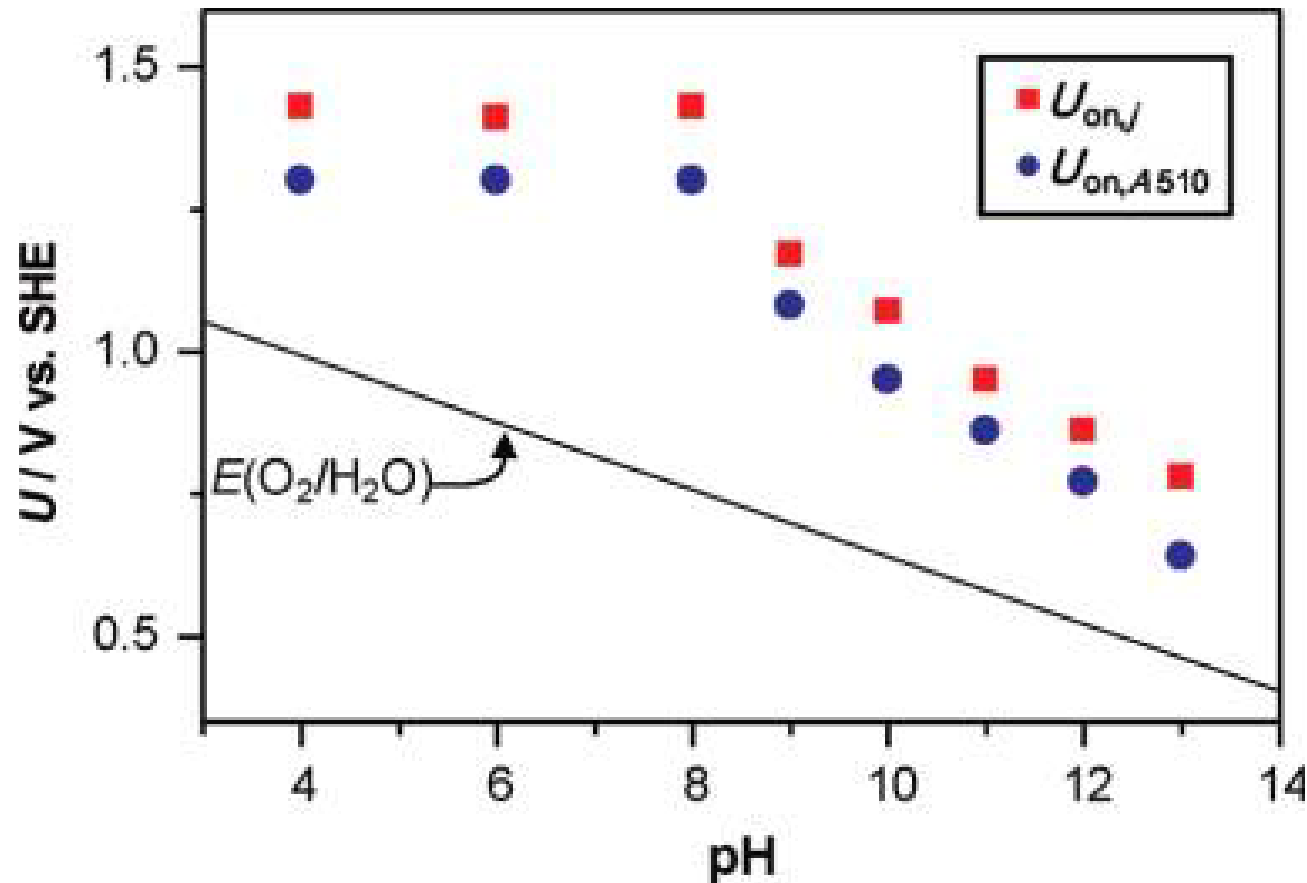


From Hydrogenics' homepage:

HySTAT® 10 – 10

10 Nm³H₂ h⁻¹, 5.4 kWh/Nm³ H₂

Oxygen evolution vs pH on MnO_x



$U_{on,j}$ is the onset potential of the OER in mixtures of aqueous NaOH and H_2SO_4 at 30 °C. $U_{on,A510}$ is the onset of the optical spectral line of Mn^{3+} on electrode surface taken as a (probably false) indication of Mn^{3+} being efficient electrocatalyst.

From: T. Takashima et al., Mechanisms of pH-Dependent Activity for Water Oxidation to Molecular Oxygen by MnO_2 Electrocatalysts, J. Am. Chem. Soc., 2012, **134**, 1519